

ASPHALT MONOMER REACTIONS

By

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I. INTRODUCTION

Asphalt has been used in a variety of ways since ancient times. Archaeologists discovered that asphalt had been used as an adhesive for building stones and paving blocks as early as 3800 B.C. These early asphalts were obtained from scattered sources formed by nature's own refining of petroleum deposits through geologic processes. (10) The 114-acre Trinidad lake and the 1000-acre Bermudez deposit in Venezuela are impressive examples of these natural processes. In the United States, a naturally occurring asphalt-like material called gilsonite is found in the Uinta River basin of Utah.

Today virtually all asphalt used commercially is manufactured from materials of petroleum origin. In order to obtain satisfactory asphalts, early refiners of this century required the use of special crude sources containing residues yielding high quality asphalts through simple distillation procedures. This limitation has largely been removed in recent years through more sophisticated procedures employing selective solvent extraction or precipitation, etc. The patent literature contains many references to the use of special chemical treatments in attempts to modify asphalt characteristics. (1) Large quantities of asphalt are made by air-blowing at temperatures in the neighborhood of 500 - 700 °F. (48)

The inherent characteristics of asphalt, together with its relatively low cost, make it ideally suited for such wide-spread

applications as road building, roofing, waterproofing and a multitude of others. The complex world in which we live today is constantly demanding new and improved materials to meet the requirements of modern applications. Asphalt is receiving a large share of the research stimulated by these demands.

A considerable amount of effort has been expended to improve asphalt properties by blending or reaction in "situ" with other materials, particularly polymeric substances, both natural and synthetic.(4, 16, 33, 42, 67, 68, 88, 93) Since 1930, interest has been shown in the effect of the addition of small amounts of natural rubber. Mealorub and Pulvatex were the first special rubber additives developed principally for this purpose. Today interest in rubber additives for paving asphalt is very high.(101) A number of vinyl compounds have been reacted with asphalts in attempts to impart better qualities.(60) Recently developed epoxy resin formulations in asphalts, having improved solvent and heat resistance, have been used quite successfully to pave jet aircraft runways and for protective coatings.(2, 3, 58)

Even though a large amount of effort has gone into the study of asphalt systems, relatively little is yet known because of the complexity of its structure. There has been recognition of distinct constituent groups present such as asphaltous acids and anhydrides, asphaltenes, asphaltic resins, petroleum resins, petroleum oils, carbenes, carboids and inorganic material.(69) Many attempts have been made by previous investigators to characterize these groups as

completely as possible with the methods available. This research has been undertaken to establish a better understanding of the fundamental aspects affecting the manner in which vinyl monomers will behave in asphalt reaction systems. This study has been approached through an analysis of factors affecting the kinetics of vinyl polymerization in asphaltic media. It is by correlation of the knowledge gained by previous investigators with the results obtained in this study, that the object of this investigation has been, in part, achieved.

II. THEORY

A. Stabilized and/or Trapped Free Radicals Are Present In Asphalts

Introduction

With the recent advent of techniques such as electron paramagnetic resonance and nuclear magnetic resonance spectroscopy, a considerable amount of effort has been focused on the study of stabilized free radicals; an area that heretofore has suffered from neglect. This neglect has stemmed mainly from the inability to make suitable measurements for proper analysis. Steacie in his review of free radical mechanisms; which appeared prior to the ability to apply these new techniques; contributed much to our understanding of active free radical processes, but did not present information of the reactive character of stable free radicals, or even of their widespread existence.(90) Since the preparation of the stable free radicals, pentaphenylcyclopentadienyl and 1,1-diphenyl-2-picrylhydrazyl, the ability of free radicals to remain dissociated has been recognized.(52, 102)

Electron paramagnetic resonance absorption probably offers the most direct means of evaluating free radical concentrations and the effects of structural configurations. A striking feature of the paramagnetic resonance spectra of stabilized free radicals is the sharpness of the absorption exhibited.(28, 59) It is sufficient to

say at this point that there appears to be little doubt as to the validity of the conclusions drawn, at least qualitatively from these measurements. (28, 47, 51, 52, 59)

Since the early discovery of stabilized free radicals, the list of compounds which exist as free radicals, per se, which form free radicals through dissociation in solution (in some cases strong electrolytes), or which may yield stable free radicals through mild oxidation with chemical or electrical means, has continued to grow. Also, the evidence for the existence of trapped and/or stabilized free radicals in many natural materials has continued to increase. At cryogenic temperatures, experiments have been devised to trap many of the more reactive free radicals.(52)

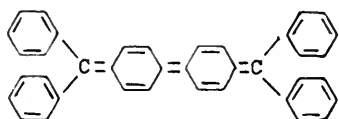
Causes of Free Radical Stability

It is obvious that a more thorough understanding of the cause of free radical stability is needed. Apparently, free radicals can be trapped through what might appear to be mechanical means. Polymerizing systems in which the polymer precipitates have been shown to occlude or otherwise trap free radicals.(53) For example, Bamford has determined that a polymer of acrylonitrile prepared at 25 °C. by photopolymerization was found to have about 8×10^{-5} gm. mole radicals per liter. This represented about 13 percent of all radicals initiated photochemically during the experiment.(13) In some materials such as dicarboxylic acids, for example, free radicals appear to be trapped by maintaining hydrogen bonds with the lattice molecules after irradiation with x-rays or gamma-rays have produced them.(5)

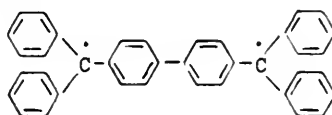
Most of the free radicals which are obtained in pure form or in solution appear to be stabilized through what is normally termed resonance. (52, 102)

It is convenient at this point to introduce the terms singlet, triplet, and bi-radical to describe concepts which will be discussed in slightly different context later in this work. An olefin or conjugated double bond system is capable of existence in a state such that all unsaturation electron pairs have the orbital spins paired. This is termed the singlet state, with only one possible combination of angular momentum vectors, because the electron spin vectors cancel. A bi-radical is visualized as the situation arising when a pair of unsaturation electrons' orbital spins become unpaired, and the electrons become distributed so that they are predominately at opposite ends of the previous olefin system. If these electrons are not physically, widely separated, then the orbital spins which are no longer paired can interact, giving rise to three possible combinations of the angular momentum vectors, with the so-called triplet state resulting. Hence, the difference between a bi-radical and triplet is one of degree. Rexroad and Gordy have illustrated these phenomena with the compound, p,p-biphenylene-bis-diphenylmethyl. (78)

Chichibabin's Hydrocarbon



Normal diamagnetic state
(singlet state)



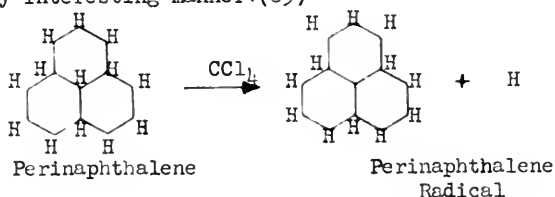
Bi-radical state
(triplet state)

The singlet, bi-radical and triplet states, are but a few of the possible electronic configurations that can exist for molecules that have complex systems of conjugated double bonds, such as condensed ring aromatic hydrocarbon systems. Indeed, most of the stable free radicals which have been cited in the recent literature have as a part of their structure multiple phenyl groups. The possibilities for resonance in these types of compounds is evident.

Free Radical Types Expected In Asphalts

The evidence for the existence of highly complicated aromatic structures; and in addition, structures containing nitrogen, oxygen and sulfur, is abundant for asphalts. This seems to be particularly true for the higher molecular weight fractions such as the asphaltenes. (34, 86, 95, 105)

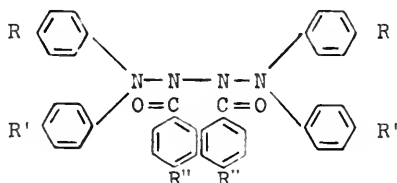
Perinaphthalene, whose structure is shown below yields free radicals in a very interesting manner.(89)



In carbon tetrachloride solutions, the central hydrogen atom is removed leaving an unsatisfied valence at this carbon atom. These conclusions were reached by examination of the fine line splitting of the electron paramagnetic resonance spectra. This solution also becomes highly colored upon standing. This type of compound is almost certain to exist in asphalt systems,

particularly the high molecular weight portion.(29, 31, 105)

Aromatic free radicals can be produced in solution by the dissociation of structures which are not tightly bound. An example of this is the dibenzoyl tetrazanes, whose generic structure is as follows:



1,1,4,4-tetra-p-alkylphenyl-2-
3-alkyldibenzoyl tetrazanes

The dissociation occurs between the central two nitrogen atoms, yielding a compound of the hydrazyl type.(87) It may be possible that analogous structures, capable of dissociating into free radicals, exist in asphalts. This has not been demonstrated to the knowledge of the author to date. Although no direct reference has been made to condensed ring aromatic compounds, other than perinaphthalene, a large number of condensed ring aromatic systems have been demonstrated to yield stable free radicals.(52)

Natural and Manufactured Materials Having Stable Free Radicals

The spectra of a large group of pyrolytic carbons, as determined by electron spin resonance (ESR), have been examined by numerous investigators. With this group of pyrolytic carbons, the high molecular weight constituents of petroleum, its residues, and other similar naturally occurring bitumens, including those derived from coal, shall also be discussed.

These materials generally exhibit sharp ESR absorption bands. Estimates of the free radical content of materials representative of this group of pyrolytic carbons has been collected in Table 1.

From the data collected in Table 1, it may be seen that stabilized trapped free radicals are, indeed, characteristic of pyrolytic carbons produced either naturally or artificially. It is clear from these data that the content of free radicals is a function of the thermal history and total carbon content. Pyrolytic carbons formed slightly below 600 °C. give the stronger ESR absorption. X-ray examination has shown that it is at the point of pronounced free radical content that the formation of condensed ring clusters begin; both with regard to the variation in formation temperature and carbon content.(12) Investigations by Austen, Ingram and Tapley have led them to suggest that:

"The essential mechanism in the trapping and stabilization of unpaired electrons [in the complex carbons being discussed] is the existence of ring clusters containing more than a certain number of carbon atoms. Such ring clusters will possess a high degree of resonance energy available for stabilization of the electrons. . . . The decrease in radical concentration above the 90 percent carbon content or 550 °C. carbonizing temperature is explained by the gradual formation of graphitic sheets, the individual carbon clusters joining and thus saturating their broken edge bonds."

In the above hypothesis, it was assumed that the radicals have been formed by the breakage of bonds around the edge of carbon clusters. It was also pointed out that some radicals may occur in packing defects producing internal trivalent carbon atoms. The ideas proposed by Austen, et al., have been generally agreed upon by other workers in the field.

TABLE 1, FREE RADICALS STABILIZED IN PYROLYTIC CARBONS

Material Source	Radical Content, Spins/gm. $\times 10^{-18}$	Treatment Temp., °C.	Weight Ratio C/H	References
<u>Coal Products</u>				
A Pittsburgh Coal	9.4		14.5	(40)
Coal Vitrain	6.5		15.3	(40)
Coal Hydrogenation Asphaltene	0.3		14.0	(40)
(In CS ₂ Solution)	4.4			
(In Dioxane Solution)	1.8			
Miscellaneous Coals	3		(60% C)	(12)
Miscellaneous Coals	40		(80% C)	(12)
Miscellaneous Coals	400		(94% C)	(12)
<u>Hydrocarbon Chars</u> ^(a)				
Dextrose Char (in vacuo)	100	570	(12, 17, 71, 96)	
Dextrose Char	2	300		(12)
Dextrose Char	20	400		(12)
Dextrose Char	70	500		(12)
Dextrose Char	70	600		(12)
Dextrose Char	30	700		(12)
Petroleum Residue Char	1	200		(12)
Petroleum Residue Char	3	400		(12)
Petroleum Residue Char	30	500		(12)
Petroleum Residue Char	15	600		(12)
<u>Amorphous Carbons</u>				
Oil Furnace Black	70-80			(56)
Channel Black	100			(56)
(Heat Treated)	280	500		(56)
(Heat Treated)	0	1200		(56)
Carbon Blacks	---	1000-1700	(b)	(52)
<u>Petroleum Products</u>				
Crude Oil Colloidal Pre- cipitate (ultracentrifuge)	8		10.9	(44)
From Miscellaneous Asphalts				
Asphaltenes	20-30		9-10	(30)
Aromatic Oils	0.5-1.0		7.6-8.2	(30)
Paraffins & Naphthenes	nil		6.0-6.2	(30)

(a) Bennet, Ingram and Tapley have shown generally that any charred hydrocarbon, when prepared slightly below 600°C., gives strong ESR absorption. (17)

(b) Ingram notes that the ESR spectra should be similar to that of hydrocarbons formed at lower temperatures, since the residence time at the high temperature is short.

An interpretation of the bond breakage at the edge of the condensed carbon rings by Ingram, is that the electron released by the bond breakage is stabilized by the large amount of resonance associated with aromatic rings, and as a result, move in highly delocalized π -orbitals over the system. The presence of such delocalized radicals has been suggested to be the cause of carbon blacks actively participating in the reinforcement of rubber.(52)

Petroleum products have been placed in the category with pyrolytic carbons because of the analogy that can be drawn between their probable origins and similar constitutions.(35) In an interesting paper by Yen, Erdman and Pollack, it was determined that the characteristic X-ray diffraction of the high molecular petroleum fraction (asphaltenes) from many crudes could be reproduced by blending samples of polyethylene and carbon blacks. Also the X-ray diffraction pattern of the aromatic portion of these asphaltenes compares with that of a blend of condensed aromatic compounds of known structure. Figure 1 is a model constructed from the data they obtained.(105) The analogy to pyrolytic carbons from other sources seems very plausible.

The paramagnetic resonance of crude oils is apparently concentrated in the high molecular weight colloidal portion. This portion has been labeled "asphaltenes" from a comparison of these materials with the so-called asphaltenes obtained from asphalts by precipitation with light paraffin hydrocarbon solvents. Gutowsky, et al., observed that the ESR absorption of a crude oil disappeared

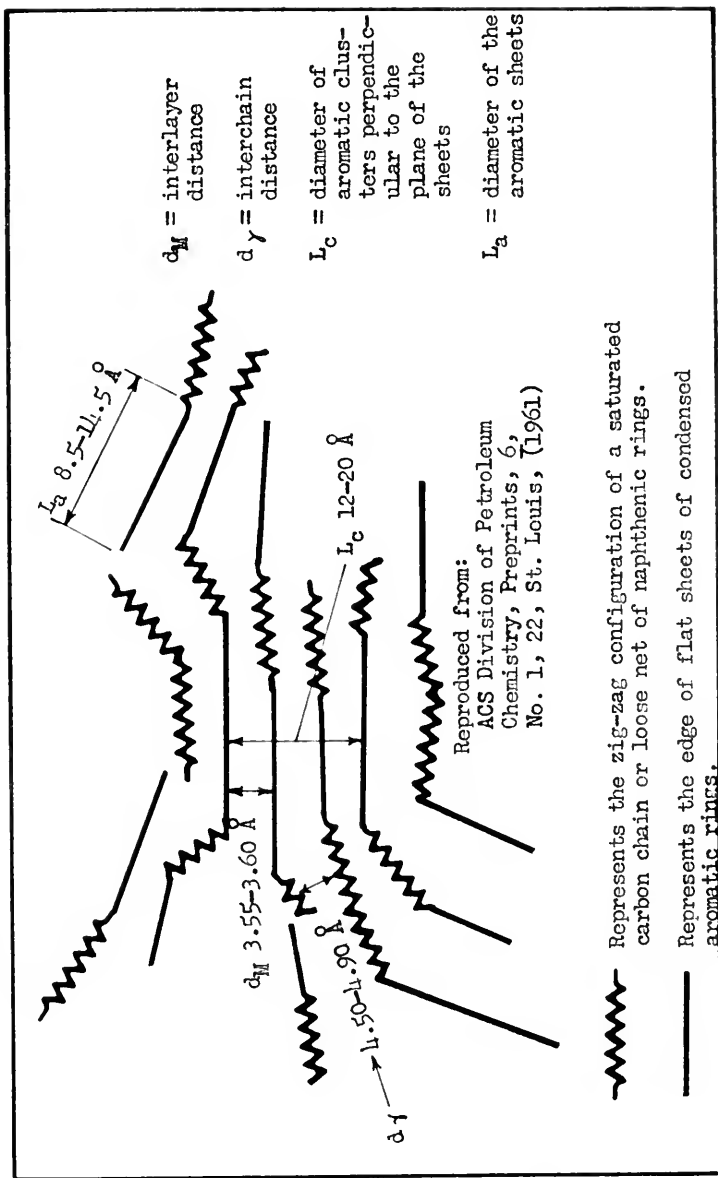


Figure 1, Cross sectional view of an asphaltene model.

after extensive centrifugation at 80,000 G's.(25, 44) Some concern has been expressed as to the possibility of the paramagnetic resonance of petroleum stemming from other than free radical sources. Vanadium in the $+1$ valence state as vanadyl readily forms chelate compounds which exist frequently in nature as porphyrins.(70) This may be true for other metals as well, and therefore, the possibility of ESR absorption from this source should not be overlooked. Eldib, Dunning and Bolen, in a study of the colloidal materials in petroleum, obtained by ultracentrifugation, have determined that vanadium and nickel are present in this colloidal material in concentrations less than 25 and 8 p.p.m. respectively.(34) These were the only metals determined to be present in appreciable concentration. O'Reilly has compared the ESR spectrum of a solid asphaltene with that of vanadyl etioporphyrin I (VEPI) dissolved in a high viscosity petroleum oil. The spectra of both samples showed the same general characteristics. The ESR absorption demonstrated by the porphyrins present in the solid asphaltenes however, is quite small compared to the band attributable to free radicals.(70) Only about 0.1 of the spin concentration observed, as determined by elemental analysis for nickel and vanadium, was attributable to these materials in asphaltenes investigated by Gutowsky, et al.(44)

In addition to the evidence cited for the presence of free radicals in asphalt, that has been essentially based upon measurements made by ESR; Poindexter has observed the Overhauser Effect in asphalt solutions. The details will not be discussed here.

However, it can be said that the contribution to proton relaxation from the asphalt is a linear function of asphalt concentration. This contribution to proton relaxation arises through the interaction of the electron spins of the free radicals with the nuclear spin of the hydrogen atoms present.(75) It was stated that there was no indication of any unusual quality of the asphalt radicals observed.

Saraceno and Coggeshall conclude from their measurements, that the free radical species in petroleum oils are stable, and are not created through dissociation of diamagnetic molecules upon dilution with solvents.(83) This is consistent with the linear contribution to proton relaxation with change in concentration as mentioned above. This however, is in contrast to the results reported for coal hydrogenation asphaltene; see Table 1. No effects on the free radical concentration were observed to be a function of either sunlight, ultraviolet light or bubbling molecular oxygen into a petroleum oil.

B. Principles Underlying Free Radical Induced Polymerization

That there are polymerization processes which are induced by the presence of free radicals does not seem to be in dispute.(14, 20, 26, 39, 77, 99) The strongest evidence for this appears to be that acceleration of polymerization rates of many vinyl compounds occurs in the presence of substances which are known to give free radicals upon thermal decomposition, after exposure to ultraviolet light, or bombardment from radioactive sources. In some cases, polymerization has been known to occur in the absence of light or free radical

forming materials. This has become known as thermal polymerization, but can still be explained on the basis of a mechanism which proceeds through the action of free radicals, once polymerization is initiated. These free radicals have generally been considered to be quite reactive, in that their life time is relatively short.

Attempts to correlate the kinetics of some of the more simple systems have been reasonably successful. A very good review of this subject has been given by Bamford and Barb.(14) It appears that the case of homogeneous solution polymerization, is the simplest to treat kinetically, particularly at relatively low concentrations of monomer. Several simplifying assumptions have usually been introduced by various authors, in the derivation of correlation equations. The main justification of these assumptions, of course, lies in the fact that they yield correlations which are experimentally true.

The overall polymerization may be described in terms of three phases which are distinct conceptually.(14, 37) These phases are initiation, propagation (in some treatments which chain transfer) and termination. During the initiation phase, several methods of opening an initial double bond have been discussed. During thermal polymerization, the assumption has often been made that a bi-molecular reaction between monomer molecules yields active free radicals. When an active free radical is formed through the action of radiation, bombardment by high

velocity particles or thermal decomposition of an unstable compound, initiation is usually assumed to occur through a bi-molecular reaction with the radical formed, and a monomer atom. During the propagation phase, the active free radicals previously formed add to the double bond of the styrene molecules in a chain fashion, with the rate of each new addition being governed by a bi-molecular reaction between the previously formed active free radical, and the new monomer molecule. Since each of the steps in this chain reaction occurs between molecular species which are very much alike chemically, even though different from one another in the absolute sense, the rate constant for each of the propagation steps is assumed to be identical. During the final or termination phase, the assumption is made that termination occurs through disproportionation and combination between any two of the existing active free radical species.

A fairly subtle effect which merits our attention is that of chain transfer with the solvent, polymer, and monomer molecules. This occurs when an active polymer radical abstracts a hydrogen atom or other atom from one of these molecules to satisfy its unsaturated valence, leaving the molecule which was attacked a free radical. If this newly formed free radical is sufficiently reactive, the effect on the overall rate of polymerization will be slight, since the propagation of the monomer reaction by this radical continues more or less uninterruptedly. Breitenbach and Maschin, also Mayo, have effectively shown this to occur when using carbon tetrachloride, a solvent ideally suited for chain transfer. By assay for chlorine

in the resulting polymer, it was found that approximately four chlorine atoms per polymer molecule were incorporated, and that the effect on the overall polymerization rate was only slight. The major effect noted for this process is a substantial decrease in the polymer molecular weight.(22, 62)

Some solvents may have a retarding effect on the polymerization rate through the action of chain transfer. This has been explained by Price and Durham on the basis of formation of stabilized solvent free radicals with insufficient reactivity to propagate continued polymer growth.(76, 98) Of the solvents studied, nitrobenzene, phenols and 2,4-dinitrochlorobenzene have been shown to have a pronounced retarding effect. In some instances as high as one dinitrochlorophenyl group per polymer chain was found when polymerization was conducted in this solvent. In each of these cases the possibilities for resonance stabilization of the free radicals is apparent.

A concept which is useful in the development of kinetic relations is the so-called "steady state".(14, 41, 90) The steady state condition can be visualized as a condition in which the rate of formation and removal of certain reactive species are approximately the same, so that a seeming equilibrium situation is manifest. Even though this is only an approximation to what is actually occurring very useful relations have been developed when the magnitude of the error introduced is small. In polymer kinetics, the assumption of "steady state" generally implies that the concentrations of the free radicals, intermediate to the polymerization process, attain

equilibrium values. From this it follows that the rate of change of a given free radical specie, with time, is nearly zero.

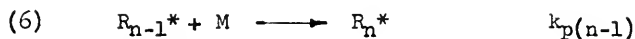
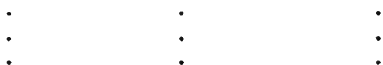
A Theoretical Equation for Thermal Polymerization

An example use of the principles cited is the treatment of the thermal polymerization of styrene in solution.(14) Experimentally, it has been shown that styrene (when quite pure) has a solution polymerization rate which is second order in terms of monomer concentration, if the reaction is not carried on to too great an extent.(8, 14, 20, 27, 43, 45, 97) This, however is not the case when polymerization proceeds in bulk, i.e., pure styrene alone. When the effect of change in the activity is accounted for, the polymerization rate is second order in terms of monomer activity. Walling, Briggs and Mayo measured the vapor pressures above various solutions of styrene and polystyrene to obtain the data required for this refinement.(97)

Bamford and Barb, in their review of polymerization processes, have presented the following mechanism for the thermal polymerization of styrene.

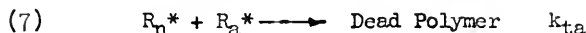
The Assumed Kinetic Mechanism for Thermal Polymerization

Equations Governing Rate	Associated Rate Constant
The Initiation Phase	
(1) $M + M \longrightarrow 2R_c^*$	k_c
(2) $R_c^* + M \longrightarrow R_1^*$	k_{pc}
The Propagation Phase	
(3) $R_1^* + M \longrightarrow R_2^*$	k_{pl}



The Termination Phase

With Active Free Radicals



Where:

M Monomer

R* Free radical

k Rate constants identified by
the proper subscripts

1,2,3,...,n,n-1 denotes the number
of monomer units affixed

c Denotes a radical formed in the
initiation phase

s Denotes a stabilized free radical

a Denotes all active free radicals

If the polymer chain length is relatively great, the overall rate will be governed by the rate of monomer reacting in the propagation steps to a fair approximation. From the preceding statement of the assumed mechanism it can be shown that the overall rate of polymerization may be expressed analytically as:

$$-d(M)/dT = k_{pc}(R_c^*)M + \sum_{i=1}^{i=n} k_{pi}(R_i^*)M \quad 1.$$

Utilizing the assumption that the k_p 's are identical and noting that,

$$R_a^* = R_c^* + \sum_{i=1}^{i=n} R_i^* ; \quad \text{by definition,} \quad 2.$$

gives,

$$-d(M)/dT = k_p(R_a^*)M \quad 3.$$

The rate of change of concentration of any free radical species may be stated in general as:

$$\text{Rate of Change} = \frac{\text{Formation Rate of Species } R_1^*}{\text{Change}} - \frac{\text{Propagation Rate to Species } R_{i+1}^*}{\text{Change}} - \frac{\text{Termination Rate of Species } R_1^*}{\text{Change}}$$

For purposes of clarity, it is shown in Table 2 through the use of material balances derived from the preceding mechanism, how these relations may be solved to obtain an equation explicit in R_a^* . Combining equation 7 from Table 2 and equation 3 yields the overall rate in terms of M.

$$-d(M)/dT = k_p (2k_c/k_{ta})^{\frac{1}{2}} M^2 \quad 4.$$

The correlation thus obtained predicts that the thermal polymerization of styrene should be second order in terms of monomer concentration. To be completely rigorous, this entire analysis should have been made on the basis of thermodynamic activity, as indicated previously, when it was stated that a correction for this must be applied in bulk polymerization. However, in dilute solution, say 10 percent monomer or less, the concentration expressed in units proportional to the number of molecules per unit volume should adequately approximate the activity. If the density does not change appreciably as polymerization proceeds in this dilute solution, a further approximation can be made; i.e., the concentration expressed in weight percent will very nearly be proportional to the concentration expressed as above.

TABLE 2, EQUATIONS DERIVED FROM THE ASSUMED KINETIC MECHANISM FOR THERMAL POLYMERIZATION AND RELATED MATERIAL BALANCES

- (1) $d(R_c^*)/dt = 2k_c(M)_c^2 - k_{pc}(R_c^*)(M) - k_{ta}(R_c^*)(R_a^*)$
- (2) $d(R_1^*)/dt = k_{pc}(R_c^*)(M) - k_{p1}(R_1^*)(M) - k_{ta}(R_1^*)(R_a^*)$
- (3) $d(R_2^*)/dt = k_{p1}(R_1^*)(M) - k_{p2}(R_2^*)(M) - k_{ta}(R_2^*)(R_a^*)$
- (4) $d(R_3^*)/dt = k_{p2}(R_2^*)(M) - k_{p3}(R_3^*)(M) - k_{ta}(R_3^*)(R_a^*)$
- (5) $d(R_n^*)/dt = k_{p(n-1)}(R_{n-1}^*)(M) - k_{pn}(R_n^*)(M) - k_{ta}(R_n^*)(R_a^*)$

Applying the steady state criterion, i.e., the summation of $d(R_i^*)/dt = 0$, and assuming that all k_p 's are approximately identical and noting eq. 2, gives,

$$(6) \quad 0 = 2k_c(M)_c^2 - k_{pn}(R_n^*)(M) - k_{ta}(R_a^*)^2$$

The second term of this equation is zero by definition of the n th term, i.e., this represents the rate of propagation of one more than the last monomer unit which is obviously zero. Therefore, by rearranging the resulting equation and solving for (R_a^*) , the following equation results.

$$(7) \quad R_a^* = (2k_c/k_{ta})^{1/2}(M)$$

Integration of the rate equation allows it to be shown that a plot of reciprocal monomer concentration versus time should yield a straight line whose slope is the overall rate constant. The details of this are shown on page 59.

C. The Influence of Stabilized Free Radicals

Previous discussion has pointed out that stabilized free radicals and/or trapped free radicals are demonstrably present in the types of materials being studied. Several investigators have noted catalytic and inhibiting effects in natural materials which are analogous to these materials under consideration.

Very recently Wright has made a careful study of the inhibiting effects of a number of pure synthetic stable free radicals and several natural materials containing free radicals.(104) During the polymerization of styrene catalyzed by benzoyl peroxide, it was found that the stable free radicals, 1,1-diphenyl-2-picrylhydrazyl and Banfield's free radical (which is prepared from Banfield's hydroxide (18)), exhibit an inhibiting effect which increased with increasing concentration. The same effect was observed for the asphaltene fraction of gilsonite and a Wilmington crude oil.(104)

Hexaphenylethane, when in solution, has been shown to dissociate into the triphenylmethyl radical.(24, 102) Mayo and Gregg, in a study of styrene polymerization, used hexaphenylethane over a considerable concentration range.(61) From material balance calculations based on the polymer molecular weight and the extent of reaction, they estimate that about 77 molecules of hexaphenylethane disappear for

each molecule of polystyrene that would have been formed in its absence. This work lead to the following conclusion:

"Any free radical may start or terminate the polymerization of a styrene chain. Whether a source of free radicals will behave as a catalyst or an inhibitor depends on the balance between the rate of addition of these radicals to monomers, the rate of interaction of radicals and the rate of growth of the polymer radicals at the chosen temperature. If the radicals do not add rapidly or if they are supplied too fast, then a high radical concentration results and chain growth is restricted. If the radicals add very rapidly, or are supplied slowly enough, polymerization will result. These statements mean simply that the dividing line between catalysts and inhibitors is not clear-cut; the differences between them are quantitative rather than qualitative."

Symons has studied the interaction between acrylonitrile and amorphous carbons and has found that oxygen-free carbons initiate polymerization in the dark.(91) With no carbon present, thermal polymerization did not occur at the temperature used, 60°C. Activation of the carbons at 400°C.-550°C. over moist air causes the initiation effect to be destroyed. This was explained on the basis of the formation of surface quinone groups which act as inhibitors. It was suggested by this author that two types of free radicals, i.e., trapped free radicals and resonance stabilized free radicals may be the active initiator. Also, the possibility of mechanically isolating some of these free radicals from the polymerization process may occur. Breitenbach and Preussler apparently confirm the work of Symons regarding the inhibiting effect of activated carbons by their study in styrene polymerization.(23) However, the inhibiting effect on styrene which does have a definite thermal polymerization rate lasted for only a limited time after which polymerization occurred at at least the normal rate. This is consistent with the concept of

inhibition by surface quinone groups since it is known that the effect of inhibition by quinones is gradually lessened through free radical reactions with quinones to give non-reactive by-products.(14, 61)

Kraus, Gruver and Rollmann studied the effect of carbon blacks on the free radical thermal polymerization of styrene at 50 °C.(55) These carbon blacks were treated in the following ways: a) reduction over platinum with hydrogen or by sodium borohydride, b) heat treatment at 1000 - 2000 °C., c) and outgassing at 300 °C. under vacuum. Each of these carbons causes a substantial induction period to occur.

(Note: The pure styrene used gave no induction period.) After the induction period, acceleration of up to five times the normal polymerization rate was obtained. Hydrogenation, presumably of the surface quinone groups present in carbon blacks, drastically reduced the length of the induction periods observed, but caused no measurable change in the acceleration effect. High temperature heat treatment destroyed both the induction period and acceleration effect. This is in accord with the known phenomenon that high temperature heat treatment causes graphitization of carbon blacks by allowing structural rearrangements that destroy stabilized free radicals.(12, 17)

Outgassing of adsorbed oxygen caused no observable changes. Free radical concentration in these carbon blacks was measured before and after polymerization. Little, if any, change in concentration (which was of the order of 10^{+18} unpaired spins per gram) occurred. This apparently negative observation prohibits it being stated conclusively that free radicals are the cause of the acceleration

observed. The possibility of this effect being produced by surface peroxide formation, however, must probably be discarded, since the thermal history with treatments up to 300 °C. had no effect.

Consideration of the ability of charcoal and other pyrolytic carbons, as well as paramagnetic substances such as free radicals, to catalyze the conversion of para-hydrogen to ortho-hydrogen points out the ability of these stabilized free radicals to interact with other systems. (82, 90)

Hulbert, et al. have considered a theoretical mechanism of vinyl polymerization from the view point of the electronic states of olefins, particularly ethylene. Their calculations indicate that ten of the twelve valence electrons in ethylene are localized by pairs taking up positions between the carbon and hydrogen nuclei. The remaining two electrons which are essentially distributed over the entire molecule, have been given the name "unsaturation electrons". (50) In the lowest energy state, these two electrons are in the same bonding orbital "N" and by the Pauli exclusion principle must then have antiparallel spins. Since these electron spin vectors cancel, there is only one possible combination of angular momentum vectors, and the so-called singlet state is the result. It is pointed out that promotion of an electron from the bonding orbital to a non-bonding orbital should be rare in the absence of an external magnetic field, because of the necessary uncoupling of the spins via exchange of magnetic energy, even though sufficient energy may be available in the molecule itself. Whenever an "odd electron molecule", i.e., a free radical, comes within the kinetic theory radius, this uncoupling

becomes more probable. The result of this uncoupling is the triplet state in which the electron spins are parallel. When parallel the spins are unpaired, in other words, what is commonly termed a diradical has resulted. This diradical may or may not have bonded with the free radical which aided in the uncoupling of the electron spins. Active diradicals once formed have been reported to be capable of propagating a chain reaction from each free radical site in the molecule.(14, 20, 26) It is not known whether or not the stabilized free radical will form a bond during the uncoupling process; however, even if the bond is formed momentarily, subsequent dissociation of this bond might occur. This possible dissociation of, or failure to form a bond could possibly account for the failure by Kraus, et al., as previously mentioned, to observe a change in the total concentration of unpaired spins before and after polymerization.

The total experience gained by the various investigators cited tends to indicate the plausibility of an acceleration effect caused by the interaction of stabilized free radicals with vinyl monomers. The ability of stabilized free radicals to remain dissociated over long periods of time does not necessarily imply that they are completely unreactive. For example, diphenylpicrylhydrazyl is known to react with more reactive free radicals even though alone it remains dissociated for long periods of time. From the ability of styrene to undergo thermal polymerization, it is clear that formation of active free radicals is possible even in the absence of catalytic

substances. The assumption of the initiation of styrene polymerization through a bi-molecular collision of styrene molecules has successfully correlated the kinetics of the thermal polymerization of styrene, it may be recalled.

Realizing that even a slight increase in the probability of forming the diradical state of styrene would increase the overall polymerization rate, and that a stabilized free radical can potentially increase this probability, leads one to the following speculation: may not the presence of a stabilized free radical, near a monomer molecule, at the time of interaction with a third molecule (which possesses a definite probability for reacting), increase this probability through the mechanism described by Hulbert? An alternative question is: may there perhaps be insufficient energy normally available for the stabilized free radicals present in asphalts to react alone with a monomer or active free radical molecule?

A Theoretical Equation for Polymerization Influenced by Stabilized Free Radicals

A mechanism which embodies the assumptions and principles utilized previously for the derivation of a rate equation correlating the thermal polymerization, has been developed for polymerization influenced by the presence of stabilized free radicals. In addition to the assumptions made previously, it has also been assumed that (1) during the initiation phase, the formation of active free radicals may occur through a ter-molecular reaction involving the stabilized free radical and two monomer molecules and (2) during

the termination phase, reaction ceases through a ter-molecular reaction involving an active free radical, a stabilized free radical and a monomer molecule. The assumed mechanism follows.

The Assumed Kinetic Mechanism for Polymerization Influenced by Stable Free Radicals

Equations Governing Rate	Associated Rate Constant
The Initiation Phase	
(1) $M + M \longrightarrow 2R_c^*$	k_c
(2) $R_s^* + M + M \longrightarrow M + R_c^*$	$k_s^{(a)}$
(3) $R_c^* + M \longrightarrow R_1^*$	k_{pc}
The Propagation Phase	
(4) $R_1^* + M \longrightarrow R_2^*$	k_{p1}
(5) $R_2^* + M \longrightarrow R_3^*$	k_{p2}
(6) $R_3^* + M \longrightarrow R_4^*$	k_{p3}
$\begin{array}{c} \cdot \\ \cdot \\ \cdot \end{array}$	$\begin{array}{c} \cdot \\ \cdot \\ \cdot \end{array}$
(7) $R_{n-1}^* + M \longrightarrow R_n^*$	$k_{p(n-1)}$
The Termination Phase	
With active free radicals	
(8) $R_n^* + R_a^* \longrightarrow \text{Dead Polymer}$	k_{ta}
With stabilized free radicals	
(9) $R_n^* + R_s^* + M \longrightarrow \text{Dead Polymer}$	k_{ts}

(a) The concentration dependence of the rate in this step is assumed to be non-linear in R_s^* . Therefore, the forward rate equation for this step is arbitrarily written as:

$$d(R_c^*)/dT_{\text{forward}} = k_s(R_s^*)^D (M)^2$$

The exponent D has been introduced to represent a simple non-linear function.

For purposes of clarity, it is shown in Table 3 through the use of material balances derived from the preceding mechanism how these relations may be solved to obtain an equation explicit in R_s^* . Combining equation 7, Table 3 with equation 3 previously shown in the discussion of thermal polymerization for the overall rate in terms of R_s^* and M yields:

$$-d(M)/dT = k_p k_{ts} / 2k_{ta} \times \left[\left((R_s^*)^2 + \frac{4k_{ta}}{k_{ts}^2} (2k_c + k_s (R_s^*)) \right)^{\frac{1}{2}} - R_s^* \right]^2 M \quad 5.$$

Setting the term in front of M^2 equal to K yields an overall rate constant that is analogous to that obtained for the thermal polymerization process, in that it is a correlation constant for an equation second order in monomer concentration.

The overall rate constant, K , is therefore, actually a function of the parameter R_s^* . This of course means that K will not be a constant unless the concentration of R_s^* remains essentially constant during a given polymerization run. This will be approximately true for polymerization that represents a small quantity of monomer polymerized. As before, the rate equation may then be integrated to show that a plot of reciprocal concentration versus time yields a straight-line curve whose slope is the rate constant K . At a concentration of $R_s^* = 0$, the rate constant, K , obviously reduces identically to the thermal polymerization rate constant.

It is believed that the preceding discussion constitutes a reasonable justification for the assumptions that have been used. At

TABLE 3. EQUATIONS DERIVED FROM THE ASSUMED KINETIC MECHANISM IN THE PRESENCE OF STABILIZED FREE RADICALS AND RELATED MATERIAL BALANCES

$$(1) \quad d(R_c^*)/dT = (2k_c + k_s(R_s^*)^D)(M)^2 - k_{pc}(R_c^*)(M) - k_{ta}(R_c^*)(R_a^*) - k_{ts}(R_c^*)(R_s^*)(M)$$

$$(2) \quad d(R_1^*)/dT = k_{pc}(R_c^*)(M) - k_{p1}(R_1^*)(M) - k_{ta}(R_1^*)(R_a^*) - k_{ts}(R_1^*)(R_s^*)(M)$$

$$(3) \quad d(R_2^*)/dT = k_{p1}(R_1^*)(M) - k_{p2}(R_2^*)(M) - k_{ta}(R_2^*)(R_a^*) - k_{ts}(R_2^*)(R_s^*)(M)$$

$$(4) \quad d(R_3^*)/dT = k_{p2}(R_2^*)(M) - k_{p3}(R_3^*)(M) - k_{ta}(R_3^*)(R_a^*) - k_{ts}(R_3^*)(R_s^*)(M)$$

$$\begin{array}{c} \cdot \\ \cdot \\ \cdot \end{array} \quad \begin{array}{c} \cdot \\ \cdot \\ \cdot \end{array}$$

$$(5) \quad d(R_n^*)/dT = k_{p(n-1)}(R_{n-1}^*)(M) - k_{pn}(R_n^*)(M) - k_{ta}(R_n^*)(R_a^*) - k_{ts}(R_n^*)(R_s^*)(M)$$

Applying the steady state criterion, i.e., the summation of $d(R_i^*)/dT = 0$, and assuming that all k_p 's are approximately identical and noting eq. 2, gives,

$$(6) \quad 0 = (2k_c + k_s(R_s^*)^D)(M)^2 - k_{pn}(R_n^*)(M) - k_{ta}(R_a^*)^2 - k_{ts}(R_a^*)(R_s^*)(M)$$

The second term of this equation is zero by definition of the n th. term, i.e., this represents the rate of propagation of one more than the last monomer unit which is obviously zero. Therefore, by rearranging the resulting equation, and solving for (R_a^*) by the quadratic formula, the following equation is obtained.

$$(7) \quad R_a^* = M(k_{ts}/2k_{ta}) \left[((R_s^*)^2 + (4k_{ta}/k_{ts}^2)(2k_c + k_s(R_s^*)^D))^{\frac{1}{2}} - R_s^* \right]$$

this point, the theoretical development of a rate equation has been completed which correlates the variation in monomer and stabilized free radical concentrations.

III. EXPERIMENTAL

A. Materials Used

Petroleum Residues

The four asphaltic residues used in this investigation were supplied through the courtesy of the Texas Company. These residues represent different types of asphalt sources that yield products having different properties. Of these asphalts, several were selected for modification by the processes of air-blowing and selective solvent removal of the asphaltene fraction.

The air-blown asphalt (R60-11) was prepared by bubbling air through a 5 kilogram batch of the Gulf Coast Naphthenic Residuum (S119) for a period of 14 hours at 500 ± 5 °F. in a stainless steel heated and vented vessel.

The asphaltene free asphalts were prepared from the filtrates, described in the following section discussing asphaltene preparation, by stripping the solvent (n-pentane) to a final temperature of about 350 °F. at 1 cm. Hg absolute pressure.

The properties which have been determined for these materials are presented in Table 4.

Petrolatum

Vaseline, a product of Chesebrough-Ponds, Inc., obtained from a local pharmaceutical supplier was used.

TABLE 4, PROPERTIES OF THE PETROLEUM RESIDUES STUDIED

Identification	S119	S61-1	R60-11	S118	S120	S61-12	S117
		Asphaltene Free S119 (n-pentane pptn.)	S119 Air Blown at 500°F. for 14 hours	South Texas Heavy As- phalt Base Residuum	East Asphaltene Central Free S120 Texas (n-pentane pptn.) Residuum		East Texas Asphalt Base Residuum
Material	Gulf Coast Naphthenic Residuum						
Kinematic Viscosity, cs.							
210°F.	289	195 too hard	153	1345	136	1633	
350°F.	18.2	16.1 > 500	8.1	43.6	11.8	54.4	
Density 77°F., gm./ml.	0.963	0.956	0.980	0.979	1.017	0.981	1.016
Pen 77°F. 100/5	too soft	too soft	15	too soft	195	too soft	227
Softening Point, R&B, °F.	too soft	too soft	261	78	108	too soft	112
% Asphaltenes(a) (n-C ₅ H ₁₂ insoluble)	2.6	0.3	39.4	1.5	21.4	0.3	24.0
% Sulfur	0.88			0.60	3.49		5.11
Component Analysis (b)							
% Asphaltenics	16.7			6.9	37.6		43.0
% Saturates	64.8			46.1	37.1		38.9
% Cyclics	18.2			47.1	25.3		18.2

(a) Determined by the method of Hubbard, R. I. and Stanfield, K. E., The Analyst, 74, 470 (1949).
 (b) Determined by the method of Traxler, R. N. and Schweyer, H. E., Oil Gas J, 51, 109 (1953).

Petroleum Asphaltenes

The asphaltenes were prepared from the stock indicated by the following procedure:

- a) Shake a mixture of the petroleum residue and n-pentane (1:1 weight ratio) until the solution is judged to be homogeneous. This was actually accomplished by allowing several days mixing in a bottle supported on moving rollers.
- b) Dilute a portion of this mixture to give a final solvent to asphalt weight ratio of 20:1 in one-gallon batches.
- c) Filter the solution on a large dense filter paper, retaining the filtrate and filtered material.
- d) Allow the filtered material to dry, free of pentane, by spreading the filter paper out flat, exposed to the air.
- e) Combine the filtrate with previous portions obtained for future stripping of the solvent under vacuum conditions.

No attempt was made to wash the asphaltenes thus obtained free of adhering substances, since the purpose here is to obtain a large quantity of the asphaltene fraction from each material rather than to obtain a strictly quantitative separation as is possible in one of the standardized analytical procedures.

Figure 2 shows the results of a series of determinations based on smaller quantities of material for the asphalt S119. It can be shown from this figure that at a solvent to asphalt ratio of 20 ml. n-pentane per gm. asphalt, a definitely large decrease in the yield

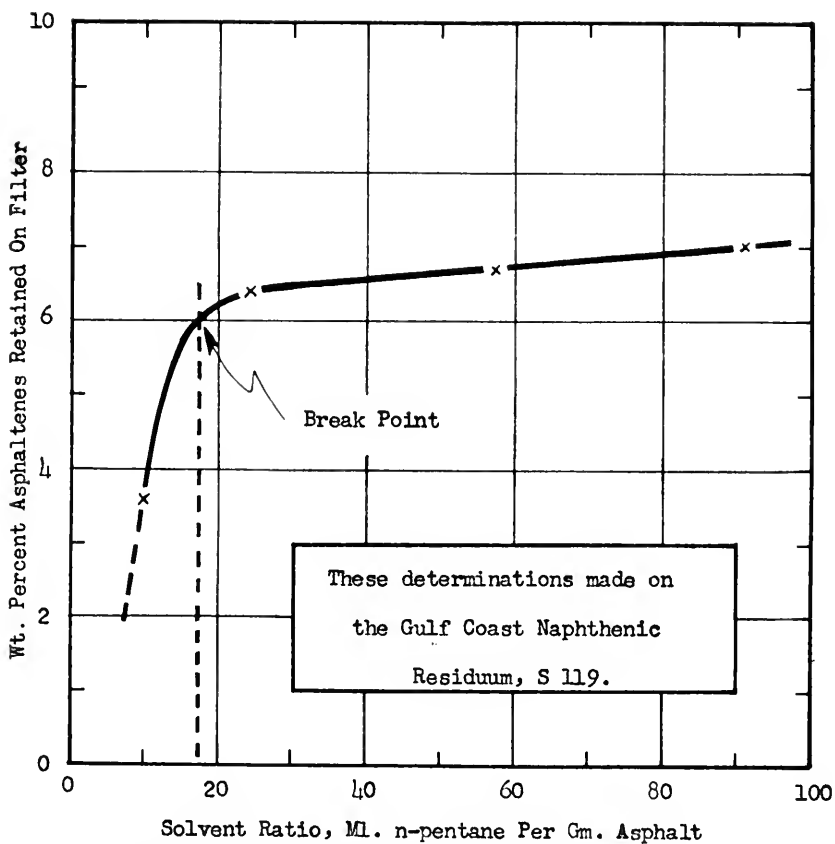


Figure 2, The influence of solvent ratio on the yield of petroleum asphaltenes.

of asphaltenes occurs. For this reason, the ratio of 20:1 on a weight basis, which is obviously somewhat greater than the above value, was used in the asphaltene preparative procedure, as a compromise between the loss of quantitateness in yield and the necessity of handling extremely large quantities of solution.

Monomers

The monomers used were obtained from the Borden Chemical Company, Monomer-Polymer Laboratories at intervals to assure that fresh materials were being used. Generally, the inhibitor (hydroquinone) was removed by washing twice with two percent NaOH solution and rinsing thrice with distilled water to a neutral point indicated by phenolphthalein indicator. Drying and removal of trace polar materials (oxygenated impurities, etc.) is accomplished by percolation through a column containing a section of granulated calcium chloride and 80-200 mesh activated alumina.

To determine if additional purification of the monomer by distillation would change the thermal polymerization rates, simple vacuum distillations at 120 °F. and 1 cm. Hg absolute pressure, using a modified vigreux column, were twice performed on a styrene sample. No change was observable.

The monomers used have been styrene, vinyl-2-ethylhexanoate and α -vinylnaphthalene.

By precipitation of polymer from the styrene used, with anhydrous methanol, it was judged that less than 0.5 percent polymer was present.

Laboratory Reagents

In all cases, commercially obtainable reagent grade chemicals have been used. It is considered that the following materials warrant special consideration:

- a) Xylene (mixed o, p, and m isomers) was found to be only suitable in the best grade (Baker's White Label Analyzed Reagent) obtainable, because of the presence of trace quantities of materials which are slowly hydrogenatable in the inferior grades.
- b) The palladium hydrogenation catalyst, Grade 937, was furnished by the Davison Chemical Company, Baltimore, Maryland. This catalyst comprises 5 percent palladium on a carbon support.
- c) The methyl alcohol used in determination of polystyrene was supplied anhydrous in one-pint, sealed bottles to assure that the presence of water was minimized.
- d) Adsorption alumina, 80-200 mesh, was purchased from Fisher Scientific Company.

B. Apparatus Description and Operation

Polymerization Equipment Description

Reactions of asphaltic and monomeric materials are conducted in a sealed autoclave which rocks to agitate the reactants. This type of apparatus provides a means of reaction in the dark, i.e., the effect of the catalytic action of light is eliminated. This reactor is equipped with a temperature controller ($\pm 2^{\circ}\text{F.}$) and

recorder which allows reactions to be conducted over long periods of time with a minimum of personal attention necessary from the operator; however, this should not be construed to indicate that neglect may be permitted. The apparatus is shown in Figure 3. It may be noted that a nitrogen cylinder equipped with pressure reducer is used to maintain pressure on the system. A list of the principal equipment follows:

- 1) American Instrument Company super atmospheric pressure rocking autoclave, 4-3/8 inch series, equipped with 3 liter and 1.5 liter bombs.
- 2) Brown Pulse Pyrovan temperature controller, 0-800 °F. range, Model No. 105C4PS-25, Serial No. 700196.
- 3) Bristol Company temperature recorder, 0-1000 °F. range, Model No. 12PG560-21, Serial No. 561908.

Auxiliary equipment is provided which allows introduction of monomer and removal of reaction samples whenever desired. Measurement and control of temperature is obtained by means of two thermocouples inserted into a well provided in the center of the autoclave. A small water-cooled heat exchanger is provided on the outlet line to cool samples immediately as they are withdrawn from the reactor.

Polymerization Equipment Operating Procedure

To charge the bomb, it is removed from the rocker, opened and stood on end with the opening upward. The desired amount of asphalt

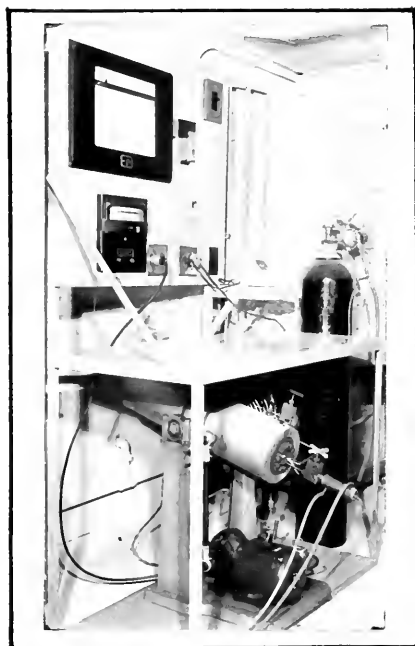


Figure 3, Polymerization Equipment

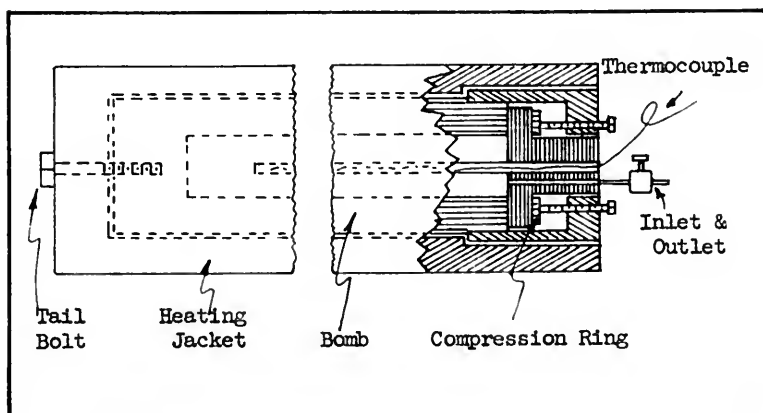


Figure 4, Bomb Assembly

and solvent is placed in the bomb, the bomb is then closed and the compression bolts tightened. Particular care must be exercised in seating the cylinder gasket to avoid scoring or otherwise damaging it. The compression ring should always be turned with the same side facing the bolts so that the opposite side will remain smooth. This may be accomplished by noting which side of this ring has been previously scarred by the bolts. The bolts should be tightened evenly by pulling them down in a "criss-cross" fashion to a torque of about 20 ft.-lbs. which is ample to seal 6000 p.s.i., as stated by the manufacturer. The bomb assembly should be put together as shown in Figure 4. It is necessary that the retaining bolt be fastened securely after placing the bomb in the rocker.

After completely assembling the apparatus and all auxiliary equipment, nitrogen is allowed to flow through for about five minutes to completely purge air from within. Then the heater, controller, shaking mechanism, etc. are turned on to bring the apparatus to the desired temperature and allowed to reach thermal equilibrium. During the run, occasional adjustment of the controller set point may be necessary. After the reactor has reached equilibrium temperature, the monomer is added via the sample outlet by forcing it into the reactor with slight pressure from the nitrogen tank. Finally, the pressure is adjusted to 100 p.s.i.g. by the reducing valve at the nitrogen tank. Samples are taken at intervals during the run and stored in a refrigerator to prevent further polymerization. It is necessary to lower the outlet end of the shaking mechanism when removing samples.

C. Analytical Methods

Determination of Monomer by Hydrogenation

A considerable amount of effort was expended to establish a suitable means of determining the concentration of the reactants, i.e., vinyl-monomers in the complex asphalt systems encountered. Quantitative selective hydrogenation has been found to be a reliable method of analysis. Because of the nature of asphalts the more common methods of olefin analysis were discarded for at least one or more reasons.

The following is a list of possible methods of analysis which might appear to be feasible, but which were discarded by at least the reasons indicated:

- a) Spectroscopy - Asphalts are essentially opaque to the regions of the spectrum which are applicable to these methods with the materials used. (15, 20, 31, 36, 65, 86, 94)
- b) Halogenations - Either interfering reactions with high molecular weight aromatics, sulfur, oxygen and nitrogen containing compounds; or subsequent splitting out of the hydro-halogens occur. Difficulty is encountered because of the necessity of using polar solvents to dissolve the redox reagents used, which are incompatible with asphalts, thereby causing precipitation to occur. (11, 21, 38, 63, 64, 66, 81)

- c) Aqueous phase addition reactions - Apparently all aqueous systems must be discarded because of the occurrence of the problem of mass transfer in the heterogeneous system resulting from the precipitation of the asphalts into a separate phase.(54)
- d) **Dilatometer** techniques - The expense of manufacturing high-pressure **dilatometers** capable of operation at a precise temperature over the wide range of temperature desired is prohibitive and the ability to obtain precise results with systems containing only 1-10 percent monomer is questionable.(20, 79, 104)
- e) Viscosity methods - These methods would not be applicable because no direct comparison could be made between the various asphalts encountered, which is part of the object of this research.(20, 32)
- f) Removal of polymer by precipitation - It has not been possible to discover a solvent which will precipitate the polymer from solution without precipitating the asphalts also.(20)

The above list is included principally to justify use of the procedure of analysis adopted. This procedure, namely a selective micro-hydrogenation, is actually quite reliable but very time consuming and tedious to perform.

Selective hydrogenation of olefins over palladium has been used by several investigators.(19, 64, 100) However, materials containing

aromatic carbonyl, nitrile and nitro groups may exhibit interference. (6, 64) The procedure described here is essentially a modification of that described by Mitchell. (64) Low blank values have been found when hydrogenating the various asphalts in the absence of vinyl-monomers, indicating that the procedure followed is quite selective for olefins in the systems encountered. Tables 5 and 6 indicate that of all materials studied, only the asphaltenes may be expected to interfere in this analysis. In all cases, the asphaltenes have been present (when removed from the asphalt) in less than 20 percent concentration. Therefore, approximately 3×10^{-6} gm. moles hydrogen per gm. sample will be used by the asphaltenes in the maximum situation.

Refer to Figure 5, a photograph and Figure 6, a schematic diagram of the equipment used to obtain details of the equipment construction. The analytical procedure used is as follows:

- a) Weigh accurately a quantity of sample which will take up from 75 to 100 ml. of hydrogen into the appropriate container. This is the sample boat shown in Figure 6 in the case of asphalt samples and the Victor-Meyer type bulb in the case where calibration with pure olefin is desired. The use of the open boat allows some evaporation and loss of the volatile constituents of the sample. This can be minimized by diluting fluid samples with 5 to 6 ml. of the solvent xylene after they have been weighed.
- b) Place 50 ml. of xylene, approximately 0.05 gm. of the palladium hydrogenation catalyst, the magnetic stirring

TABLE 5, HYDROGENATION BLANK VALUES FOR SEVERAL ASPHALTS

Test Conditions: Hydrogenation over palladium catalyst at room temperature and pressure for at least eight hours.

Designation	Description	Gm. Moles Hydrogen Per Gm. Sample	Equivalence in Weight % Styrene
S117	East Texas Asphalt Base Residuum	7.5×10^{-5}	0.078
S118	South Texas Heavy Asphalt Base Residuum	5.3×10^{-6}	0.055
S119	Gulf Coast Naphthenic Residuum	$< 10^{-6}$	< 0.010
S120	East Central Texas Residuum	6.6×10^{-6}	0.068
S61-1	Asphaltene free S119	$< 10^{-6}$	< 0.010
S61-12	Asphaltene free S120	$< 10^{-6}$	< 0.010
R60-11	Air Blown S119	$< 10^{-6}$	< 0.010

TABLE 6, HYDROGENATION BLANK VALUES FOR TWO ASPHALTENES

Test Conditions: Hydrogenation over palladium catalyst at room temperature and pressure for at least eight hours.

Designation	Description	Gm. Moles Hydrogen Per Gm. Sample	Equivalence in Weight % Styrene
S61-6	Asphaltenes from S119	1.2×10^{-5}	0.125
S61-9	Asphaltenes from S120	9.9×10^{-6}	0.100

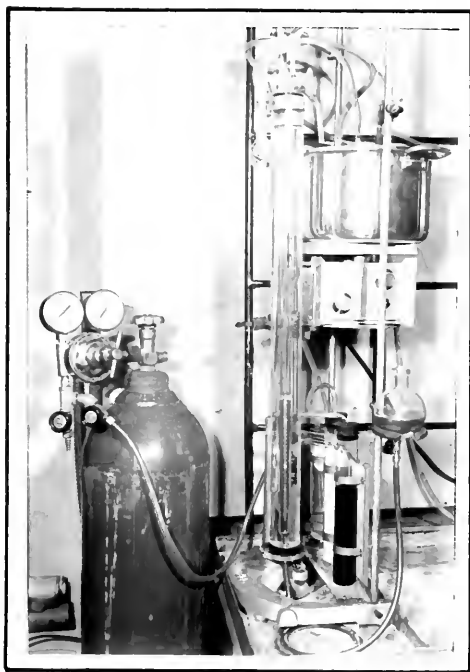


Figure 5, Selective catalytic micro-hydrogenation assembly.

- bar, and the sample container into the reaction vessel as shown in Figure 6 and assemble the apparatus.
- c) Purge the burette of air and fill it with hydrogen. Turn on the stirrer and water, and adjust the valves so that hydrogen will flow through the reaction vessel to purge it of air. About 30 minutes has been found sufficient to reduce any oxide on the catalyst and saturate the solution with hydrogen so that no further up-take of hydrogen

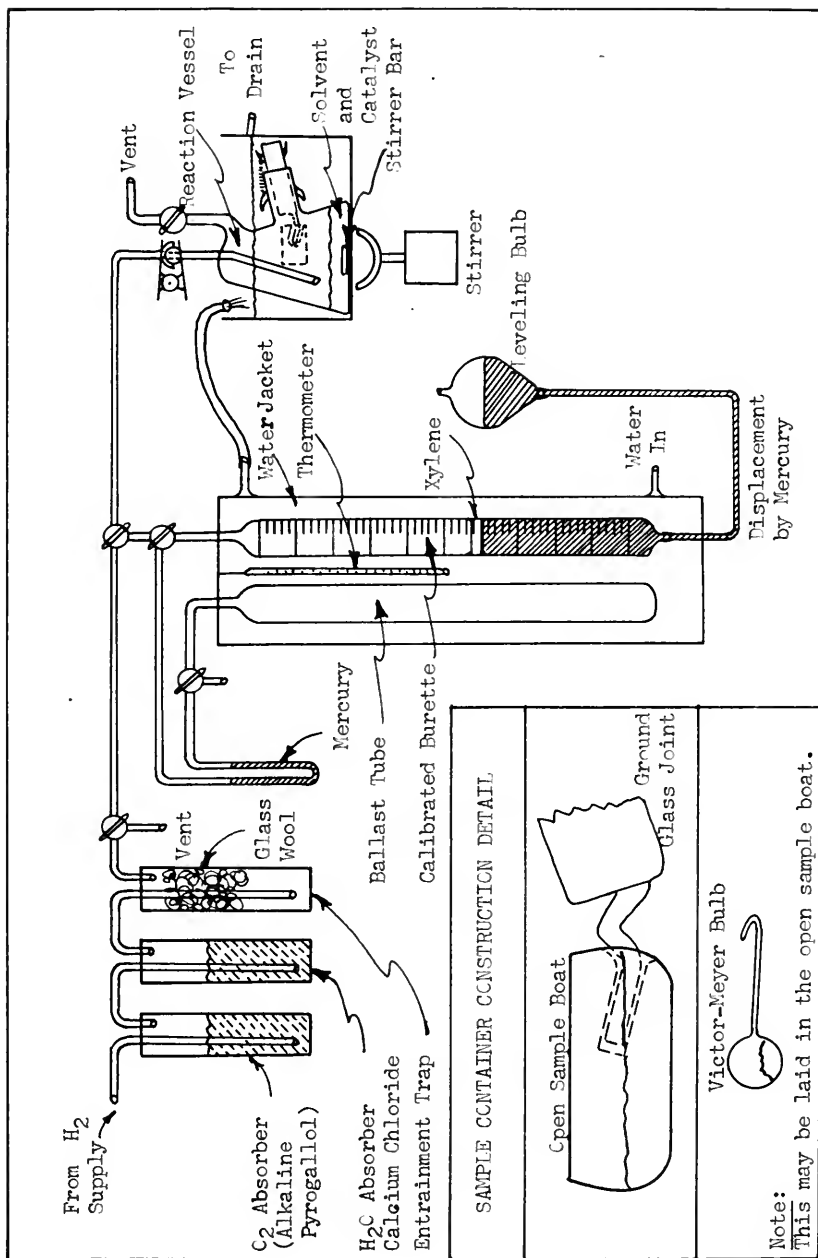


Figure 6, A schematic diagram of the hydrogenation apparatus.

occurs. A longer time should be avoided because of sample evaporation.

- d) Vent the ballast tube to the atmosphere, fill the burette with hydrogen, adjust the valves to connect the burette with the reaction vessel and obtain an initial burette reading; checking to make sure that the pressure in the ballast tube is balanced by the pressure in the burette via the manometer. Close both vents and empty the sample containers into the solvent by rotating the ground-glass joint which supports the sample boat. The Victor-Meyer bulb, when used, may be broken against the open sample boat by gently shaking the reaction vessel which is connected to the burette by a flexible coupling. Obtain the atmospheric pressure and water temperature.
- e) Occasional adjustment of the level of the mercury in the burette is necessary to avoid large pressure differentials which would otherwise cause leaks to develop. After completion of the hydrogenation (this is judged by the end of hydrogen up-take), obtain the final burette reading after adjusting the pressure to that in the ballast tube by means of the leveling bulb. Usually about two to three hours is required for completion of the analysis after complete solution of the sample is achieved. Because of the shape of the sample boat, the hydrogenation catalyst tends to gradually accumulate in it. It is therefore

necessary to occasionally shake the reaction vessel to remove this accumulation (about each one-half hour).

Other Methods of Olefin Analysis

Several other test methods were devised for analysis of olefins, particularly styrene, and used to check the accuracy of the hydrogenation procedure. A monomer volatility test, a test employing quantitative precipitation of the polymer formed and a bromination test will be discussed.

The Volatility Test

The purpose of this test is to evaluate the amount of unreacted monomer remaining in the samples of monomer-polymer-asphalt mixtures resulting from reactions occurring in monomer-asphalt systems. It is generally to be assumed that only the unreacted portion of the monomer is determined. However, this is necessarily only an approximation because of inherent test limitations. The principle involved is that of the removal by vacuum distillation of the volatile portion (monomer) from a suitably arranged sample at an appropriate temperature and pressure.

A constant temperature oven large enough to contain a large sized vacuum dessicator provided with shelves or a high vacuum oven is required for heating the samples. The samples themselves are contained in the bottom half of 10 cm. diameter petri dishes covered with watch glasses turned with the concavity downward. This allows any sample spattering to flow back into the petri dish rather than down the outside as would otherwise be the case.

Using reagent grade chemicals, a solution of the concentration of 1.00 gram per liter of p-t-butylcatechol dissolved in benzene is prepared to serve as an inhibitor during the test to prevent further unwarranted polymerization of the monomer.

Weigh accurately (± 0.001 gm.) an approximate 5 gm. sample into a petri dish and record the total gross weight of sample, petri dish and watch glass used for the sample. Immediately add 10 ml. of the solution of p-t-butylcatechol and allow the sample to dissolve. After solution of the sample, gently tilt the dish several times to mix the inhibitor. Place the samples in the oven at atmospheric pressure, adjusting the watch glass so as to only cover about two-thirds of the petri dish. This allows more rapid removal of the solvent.

When the samples appear nearly dry, remove them from the oven and allow them to cool to room temperature (overnight is permissible since further polymerization will be inhibited). Cover completely and again place the samples in the oven, but this time under vacuum for a period of eight hours before removing and reweighing the samples. The oven must be cold at the start to avoid sample spattering. It may be necessary to vary the temperature and pressure when removing various monomers. However, it has been found that successful removal of styrene monomer can be accomplished at 5-6 mm. Hg pressure and 200 °F.

The weight percent styrene is determined as follows:

$$\% \text{ Styrene} = \frac{100(\text{Gross wt. loss} + \text{Blank sample wt. gain})}{\text{Sample wt.}} \quad (a)$$

The Quantitative Precipitation of Polymer (20)

To 100 milliliters of anhydrous methanol in a 250 milliliter beaker add 25 gm. of sample. Stir well and place on a steam bath for five minutes to coagulate the sample. Allow the solution to cool and filter on a tared Gooch crucible. Dry under an infrared lamp for five minutes, then allow the polymer to dry to constant weight in an oven at 70 °C. Cool in a dessicator and weigh.

The weight percent styrene is determined as follows:

$$\% \text{ Styrene} = \% \text{ Styrene Charged} - \frac{(\text{Wt. polymer})(100)}{\text{Wt. Sample}}$$

It must be noted that this procedure will work only when asphalt is not present since methanol will also precipitate a portion of the asphalt.

The Bromination Procedure

Refer to the American Society of Testing Materials standard test D 1158 - 57T. (11) It must be noted that this method will work only when the asphalt is present in a small amount since it precipitates and otherwise interferes in samples which contain an appreciable amount.

A comparison of the results obtained by these methods with those obtained by hydrogenation is given in Table 7. The hydrogenation

(a) The blank is determined on an asphalt sample adding only the p-t-butylcatechol solution. A value of 0.017 gm. appears to be satisfactory as a result of the average value obtained using several samples for blank determination. Further attempt at increased accuracy is not felt justified in view of the overall accuracy of the method.

TABLE 7, A COMPARISON OF ANALYSES FOR STYRENE BY HYDROGENATION WITH OTHER METHODS

Run Number	Asphalt Used	Charge Conditions				Temperature, °F.			
		% Asphalt	% Xylene	% Styrene	% Styrene				
R60-5	S119	Elapsed time, min.							
		90	0.0	10	300				
		Wt. % Styrene (by Hydrogenation)							
R60-4	S119	Elapsed time, min.							
		90	0.0	10	400				
		Wt. % Styrene (by Volatility Loss)							
R60-3	S119	Elapsed time, min.							
		90	0.0	10	400				
		Wt. % Styrene (by Volatility Loss)							
R61-5	None	Elapsed time, min.							
		90	0.0	10	300				
		Wt. % Styrene (by Volatility Loss)							
R61-45	R60-11	Elapsed time, min.							
		90	0.0	90.0	10				
		Wt. % Styrene (by Hydrogenation)							
R61-46	R60-11	Elapsed time, min.							
		90	0.0	90.4	10				
		Wt. % Styrene (by Hydrogenation)							
R61-45	R60-11	Elapsed time, min.							
		90	0.0	90.4	10				
		Wt. % Styrene (by Hydrogenation)							
R61-46	R60-11	Elapsed time, min.							
		90	0.0	90.4	10				
		Wt. % Styrene (by Hydrogenation)							

procedure consistently gives results which are slightly low. This can be attributed to a slight evaporation of the monomer from samples during the purging phase of the hydrogenation procedure. This has also been found to be true for hydrogenation of samples which have been blended to give a known composition. The error from this source appears to be less than 5.0 percent of the total quantity of monomer present. The results obtained by hydrogenation and bromination are plotted in Figure 7 in the manner employed for the use that these data are intended. It can be seen that very reasonable agreement is obtained, even though the hydrogenation values are somewhat low.

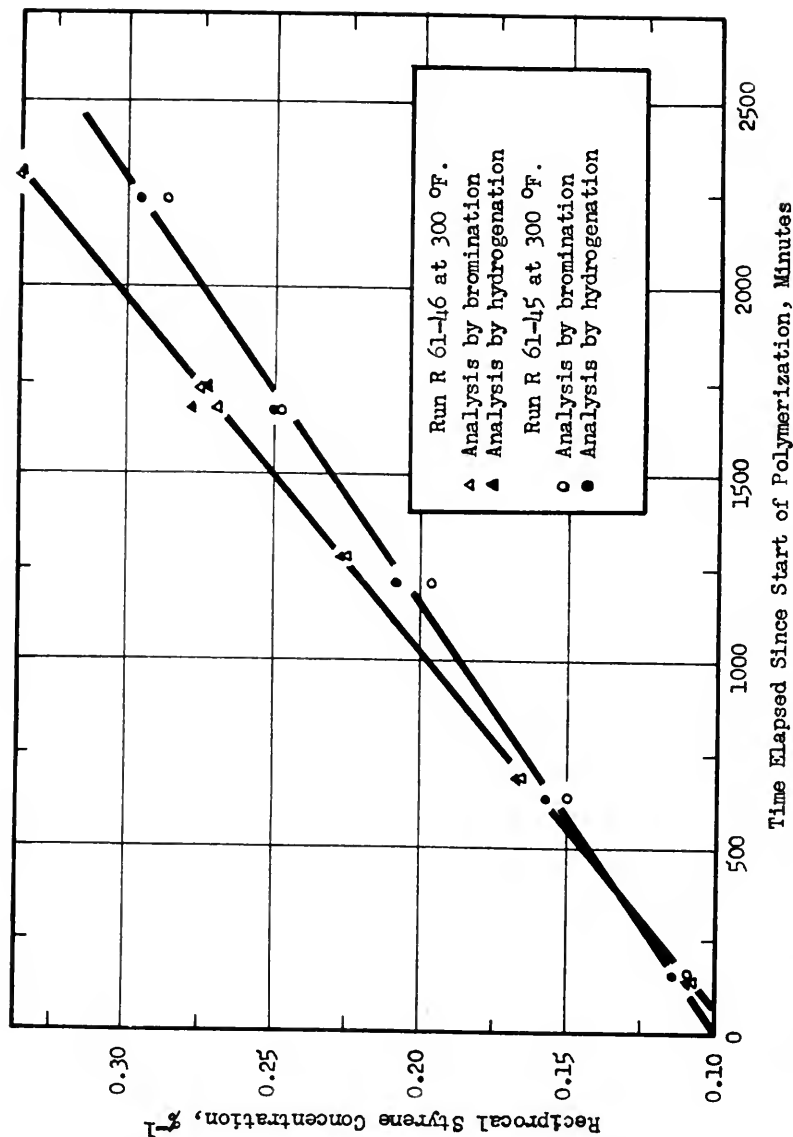


Figure 7, A comparison of the results of analysis by bromination and hydrogenation.

IV. CALCULATIONS

A. Method of Calculating Monomer Concentration

Derivation of an Equation for Calculating Monomer Concentration From Hydrogenations

Data obtained,

Initially

Burette reading
Jacket temperature
System pressure (by reference to
the atmospheric pressure)
Sample weight

Finally

Burette reading

From the ideal gas law,

$$PV = nRT$$

6.

Where: n Gm. moles of gas
P Pressure
V Volume
R Ideal gas law constant
T Absolute temperature

Rearranging gives,

$$P/T = nR/V$$

7.

$$(P/T)_{\text{ballast tube}} = (nR/V)_{\text{ballast tube}} = \text{a constant}$$

8.

(This is true for a given determination since
n and V are constant.)

Therefore,

$$(P/T)_{\text{ballast tube}} = (P/T)_{\text{hydrogenation system initial}} = (P/T)_{\text{hydrogenation system final}}$$

$$= \left[\frac{\text{barometer reading}}{\text{jacket temperature}} \right]_{\text{initial}} = (P_b/T_j)$$

9.

Where: b Denotes burette
j Denotes the jacket
i Denotes initial conditions

Note: Under the conditions in which this test is performed, use of the ideal gas law is adequately justified.(92)

Since the ballast tube provides a means of reference to a constant (P/T) ratio, minor fluctuations in the temperature of the water jacket are admissible as long as the entire apparatus is all at the same temperature. Continuously flowing laboratory tap water through the apparatus accomplishes this with no more than a 2°F. variation in temperature from beginning to end of the determination. The amount of gas disappearing may then be calculated as follows.

$$V_{h_i} = V_r + V_{b_i} \quad 10.$$

$$V_{h_f} = V_r + V_{b_f} \quad 11.$$

Where: r Denotes reaction flask
b Denotes burette
h Denotes hydrogenation system
f Denotes final conditions

From the ideal gas law and substituting from the preceding equations,

$$n_i = V_{h_i} P_i / RT_i = (V_r + V_{b_i}) P_i / RT_i \quad 12.$$

$$n_f = V_{h_f} P_f / RT_f = (V_r + V_{b_f}) P_f / RT_f \quad 13.$$

Subtracting equation 13 from equation 12 and substituting the constant ratio of (P/T) from equation 9, gives,

$$n_o = n_i - n_f = (V_{b_i} - V_{b_f}) P_b / RT_j \quad 14.$$

Where: o Denotes the change from initial to final conditions

However, since the gas is saturated with solvent vapor, a correction for this error must be applied. The proper correction factor may be determined as follows,

$$n_{H_2}/n_S = P_{H_2}/P_S \quad (\text{i.e., partial pressure law for ideal gases}) \quad 15.$$

Where: H_2 Denotes molecular hydrogen
 S Denotes solvent vapor
 p Partial pressure

The partial pressure of hydrogen is the total pressure less the solvent vapor pressure: this gives,

$$P_{H_2} = P_b - P_S \quad 16.$$

Rearranging equation 15 and substituting from equation 16, yields,

$$n_S = n_{H_2} \times \frac{P_S}{P_b - P_S} \quad 17.$$

From a material balance on the gas disappearing,

$$n_o = n_{H_2} + n_S \quad 18.$$

Note: The above is approximately true if the small fluctuation in temperature does not change the solvent vapor pressure materially.

Substituting equation 17 in equation 18 gives,

$$n_o = n_{H_2} \times \left[\frac{P_S}{(P_b - P_S)} + 1 \right] \quad 19.$$

Equating equations 19 and 14, and solving for n_{H_2} gives,

$$n_{H_2} = (V_{b_i} - V_{b_f})(P_b - P_S)/RT_j \quad 20.$$

The monomer concentration may then be calculated as follows,

$$\% \text{ Monomer} = 100 \, n_{H_2} \, m/W = 100 \, m(V_{b_i} - V_{b_f})(P_b - P_S)/RT_j W \quad 21.$$

Where: m Monomer molecular weight
 W Weight of sample hydrogenated

Determination of Solvent Vapor Pressure

In order to use the preceding equation, it is necessary to estimate the solvent vapor pressure. Several factors which will affect the exactness with which it is practical to determine this value are:

- a) The presence of sample as solute in the system. (72)
- b) The xylene used is a mixture of the o, p and m isomers which tend to vary in concentration from batch to batch.
- c) There is a slight variation in temperature over the extent of the determination.

The last two isomers of xylene noted above predominate in the mixed system. (80) For this work it has been considered adequate to use the data presented in Figure 8, which is the vapor pressure of m-xylene. (57)

Xylene was picked as a solvent because of its ability to dissolve both the asphalts used and the polymers formed, its low vapor pressure and ready availability in a grade which has no observable hydrogenation blank value. (Xylene supplier mentioned earlier.)

B. Overall Polymerization Rate Constant Calculations

Empirical Determination of the Polymerization Rate Constant

By integration of the equation developed for the polymerization process under study, an equation results which may be rearranged to give a linear plot when reciprocal concentration is the ordinate and time the abscissa.

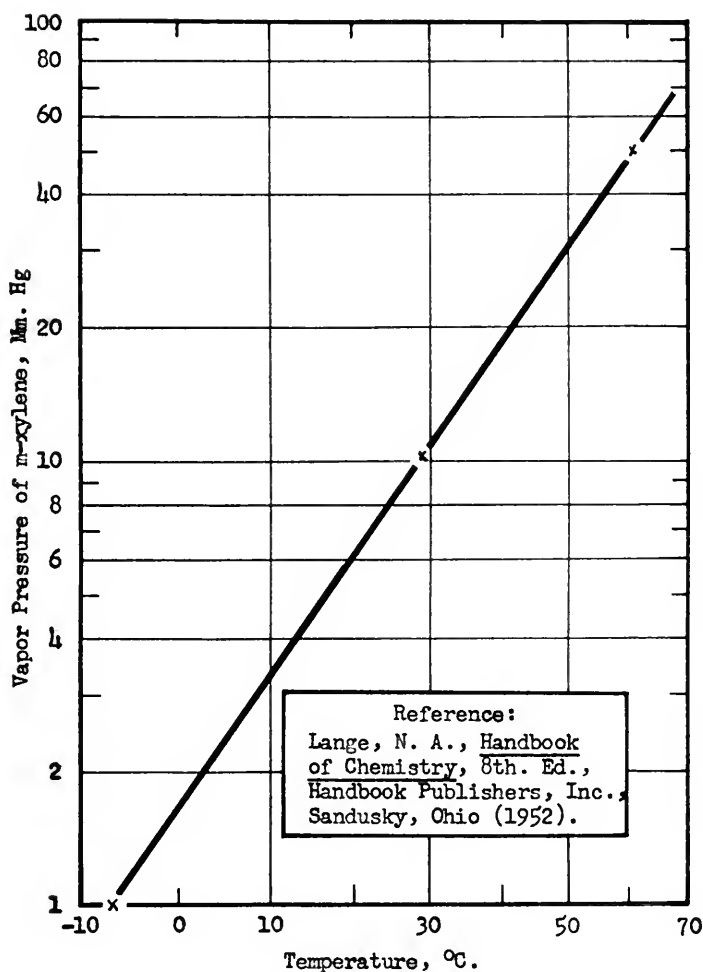


Figure 8, Vapor pressure of m-xylene

This equation is,

$$-d(M)/dT = K(M)^2 \quad 22.$$

Where K has been set equal to: (See page 29)

$$K = (k_p k_{ts} / 2k_{ta}) \left[((R_s^*)^2 + \frac{4k_{ta}}{k_{ts}^2} (2k_c + k_s (R_s^*)^D))^{\frac{1}{2}} - R_s^* \right] \quad 23.$$

By separation of the variables and integrating between the limits, $T = 0$, T , and $M = M_1$, M , the following equation may be obtained,

$$1/M = KT + 1/M_1 \quad 24.$$

Where: T Polymerization time, minutes
 M Monomer concentration, weight percent
 R_s^* Stabilized free radical concentration,
 No. free rad. per unit weight

By plotting $1/M$ versus T experimentally determined during a given polymerization run, a straight line will be obtained whose slope is identically equal to the overall rate constant. As a check upon the experimental data, the intercept of this line with the ordinate should equal the reciprocal of the monomer concentration initially charged. This calculation is illustrated in Figure 9, using the experimental data for Run 60-9.

Correlation of the Temperature Effect

Determination of the Activation Energy, H

Previous to the development of the Eyring theory of absolute reaction rates, an equation attributed to Arrhenius was generally used to evaluate the effect of temperature upon the reaction velocity constant. This equation has been found to be satisfactory to correlate experimentally determined data for a large number of systems. (49)

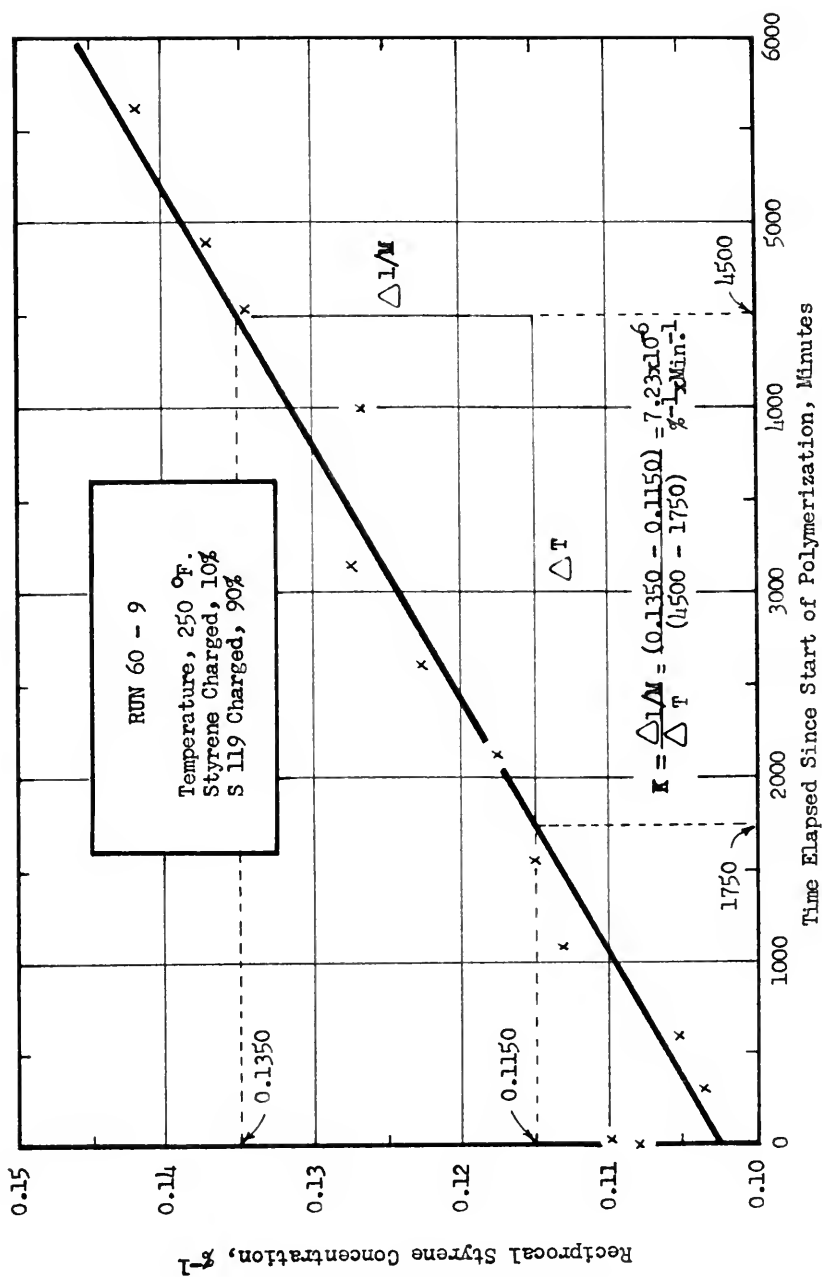


Figure 9, Calculation of experimentally determined overall polymerization rate constant.

The Arrhenius equation for correlation of the overall polymerization rate constant K is given below,

$$K = A \exp (-H/RT) \quad 25.$$

Where: A Arrhenius frequency factor
H Energy of activation

Taking logarithms of the Arrhenius equation and rearranging yields,

$$\log_{10} K = \log_{10} A - (0.4343H/R)(1/T) \quad 26.$$

Therefore, the slope of a plot of $\log_{10} K$ as ordinate versus $(1/T)$ as abscissa yields a plot whose slope N is,

$$N = - (0.4343H/R) \quad 27.$$

If R, the ideal gas constant, is taken to equal 1.104 cal. per gm. mole \times $^{\circ}\text{R}$. and T is in $^{\circ}\text{R}$., the energy of activation, H, may be determined by,

$$H = - 1.104 N / 0.4343 = - 2.542 N, \text{ cal. per gm. mole} \quad 28.$$

The numerical value of the slope, N, is determined graphically in a manner analogous to that employed to estimate the value of the overall polymerization rate constant as illustrated in Figure 9. Since the details of this calculation would be repetitious, they are omitted here.

An Absolute Basis for The Overall Polymerization Rate Constant

Theoretically to be used properly, the K of the Arrhenius equation must be expressed in some set of units which is directly proportional to the number of atoms or molecules reacting per unit volume of reaction system. From an empirical standpoint, however,

this may not be necessary and may even be misleading. Conversion of the data as obtained experimentally may involve making assumptions of quantities such as densities, etc., which introduce unnecessary error into a correlation that might be satisfactory for many purposes without applying the corrections.

The overall polymerization rate constant, K ($\%^{-1} \times \text{min.}^{-1}$), may be converted to K' in units with an absolute basis (liters per gm. mole-min.) as follows,

$$K' = c_f K \quad 29.$$

$$\text{Where: } c_f = 0.1 \frac{\text{monomer molecular weight}}{\text{solution density in gm./cc.}}$$

This may be demonstrated in the following manner,

$$\frac{100 \text{ gm. solution}}{\text{gm. monomer-min.}} \times \frac{\text{gm. monomer}}{\text{gm. mole monomer}} \times \frac{\text{cc. solution}}{\text{gm. solution}} \times \frac{\text{liter}}{\text{cc.}} = \text{liter per gm. mole-min.} \quad 30.$$

The order of magnitude of the error introduced in the energy of activation calculation as a result of neglecting the correction for density variation with temperature may be estimated. By the method previously described, N may be determined for a given system in the following manner,

$$N = \frac{\log_{10} K_{400^\circ \text{F.}} - \log_{10} K_{200^\circ \text{F.}}}{(1/T)_{400^\circ \text{F.}} - (1/T)_{200^\circ \text{F.}}} \quad 31.$$

Letting, $'$, denote a corrected value of N and K , the following is obtained,

$$N' = \frac{\log_{10} K'_{400^\circ \text{F.}} - \log_{10} K'_{200^\circ \text{F.}}}{(1/T)_{400^\circ \text{F.}} - (1/T)_{200^\circ \text{F.}}} \quad 32.$$

Sample Calculation for Runs With S 119

For the system, 10 percent styrene and 90 percent S 119, the solution densities are: 0.914 gm. per cc. at 200 °F. and 0.851 gm. per cc. at 400 °F. (Refer to Table 8) Therefore (styrene molecular weight is 104.1),

$$K_{200^{\circ}\text{F.}}^I = 0.1(104.1)(K_{200^{\circ}\text{F.}})/0.914 \quad 33.$$

$$K_{400^{\circ}\text{F.}}^I = 0.1(104.1)(K_{400^{\circ}\text{F.}})/0.851 \quad 34.$$

TABLE 8, DENSITIES OF STYRENE, S119 AND SOLUTIONS OF THESE MATERIALS

Material	Density at 77 F., gm. per cc.	Density at 200 F., gm. per cc.	Density at 400 F., gm. per cc.
Styrene	0.902(a)	0.842(a)	0.744(b)
S119	0.963(c)	0.922(d)	0.863(d)
10% Styrene + 90% S119		0.914(e)	0.851(e)

- (a) Cited in reference (7).
 (b) Extrapolation of data cited in reference (7).
 (c) Measured value.
 (d) Estimated from the cubical coefficient of expansion cited in reference (9).
 (e) Calculated assuming additivity of densities of the materials comprising the solution on a weight basis.

By reference to Figure 12, page 74, it may be found that,

$$\log_{10} K_{400^{\circ}\text{F.}} - \log_{10} K_{200^{\circ}\text{F.}} = 2.85 \quad 35.$$

also,

$$(1/T)_{400^{\circ}\text{F.}} - (1/T)_{200^{\circ}\text{F.}} = -0.000354 \text{ }^{\circ}\text{R.}^{-1} \quad 36.$$

Substituting these values and the values for density gives,

$$N' = \frac{\log_{10} K_{400}^{\circ F.} - \log_{10} K_{200}^{\circ F.} + \log_{10} (0.914/0.851)}{-0.000354}$$

$$= (2.85 + 0.0306)/-0.000354 = -8,140^{\circ} R. \quad 37.$$

The value for N determined without applying this correction is -8,060. This represents an error of,

$$\text{Percent Error} = \left| \frac{-8060 - (-8140)}{8140} \right| \times 100 = 1\% \quad 38.$$

The energy of activation determined may be expected, therefore, to be low by about one percent.

Determination of Constants for the Theoretical Rate Equation

The I. B. M. 650 digital computer has been used to calculate values of K as a function of R_S^* . By systematically varying the parameters it has been possible to obtain calculated curves that agree approximately with experimentally determined data. This discussion will be presented later in greater detail.

The program for these calculations has been written for the I. B. M. 650 by utilizing the "Flatran" system. This system, which has been developed at the University of Florida, translates the program, as written from simplified symbols analogous to those used in ordinary algebraic calculations, to the more complex language utilized by the machine computer.

The equation for the rate constant, K, has been reduced to a simpler form by substitution of symbols as follows: (See eq. 23, p. 59),

$$K = A \left[(R^2 + BR^D + C)^{\frac{1}{2}} - R \right] \quad 39.$$

by letting:

$$A = k_p k_{ts} / 2k_{ta}; \quad B = 4k_{ta} k_s / k_{ts}^2; \quad C = 8k_{ta} k_c / k_{ts}^2; \quad D = D;$$

$$R = R_s^*.$$

The Flatran Program

The Flatran program has been written in accordance with procedures defined in the Flatran Manual by Peterson.(73) This program is designed to calculate values of K in terms of R over a range of $R = 10^{-7}$ to 9×10^{-4} in increments which vary with the magnitude of R. The Flatran program follows:

```

0 0001 0 READ,A,B,C,D
0 0002 0 K#A*%SQRT%R*R%B*%R**
0 0002 1 D%&C%-R%
0 0000 0 X#0
0 0000 0 F#0.0000001
0 0000 0 PUNCH,R,K,A,B,C,D
0 0006 0 G#8*F
0 0000 0 H#2*F
0 0000 0 DO8R#F,G,H
0 0007 0 K#A*%SQRT%R*R%B*%R**
0 0007 1 D%&C%-R%
0 0008 0 PUNCH,R,K,A,B,C,D
0 0000 0 F#10*F
0 0000 0 IF#F-0.001%6,1,1
0 0009 0 STOP
0 0000 0 END

```

The machine language program compiled via the Flatran program is included in the Appendix.

C. Calculation of Relative Free Radical Concentrations

The experimentally determined data for the various asphalt systems has been plotted in the results section in the form obtained, i.e., the polymerization rate constant, K, versus the percent asphalt or asphaltene in the solutions studied. For a comparison to be made in the discussion of results section, it is desirable that the

concentration can be converted to a basis such that the stabilized free radical concentration can be compared. Experimental data has been determined to evaluate the free radical concentration in the various materials on a weight basis. Using these data, which are given Table 10, page 86, the desired comparison may be made in the following manner.

Define the ratio of free radicals in the various asphalts on a weight basis as,

$$\text{FR ratio of A:B} = \frac{\text{Free radicals per gm. A}}{\text{Free radicals per gm. B}} \quad 40.$$

D. Estimation of the Absolute Free Radical Concentration

The estimated values of the absolute free radical concentration of the various materials have been given in Table 10, page 86. If it is assumed that the free radical concentration in an asphalt or asphaltene solvent system is proportional to the asphalt concentration then,

$$R_g^* = q_A(\% \text{ Species A in the system}), \quad 41.$$

in gm. moles free radicals per kgm. of system of A

Where: q_A The specie quotient, a quantity that will cause the units of R_g^* to be, gm. moles of free radicals per kilogram of system of Species A. Species A may be an asphalt or asphaltene.

In order to obtain the concentration of R_g^* in the desired units, it is necessary to make the conversion of units from free radicals per gm. to gm. moles free radical per kgm. This may be accomplished by

the use of equation 42, which follows,

$$\frac{\text{Free Radical Conc., in gm. moles}}{\text{F.R. per kgm. sample}} \quad 42.$$

$$\frac{\text{Free Radical Conc., in}}{\text{F. R. per gm.}} \times \frac{1000 \text{ gm.}}{\text{kgm.}} \times \frac{1}{6.02 \times 10^{23}} \frac{\text{gm. moles}}{\text{molecule}}$$

Solving equation 41 for q_A gives,

$$q_A = \frac{R_s^*}{\% \text{ Species A in the system}} \quad 43.$$

The numerical value of q_A may be obtained by using the value of R_s^* corresponding to 100 percent of Species A, i. e., for the concentration of the asphalt or asphaltene with no solvent added. The specie quotients necessary for systems studied are calculated below.

(Note: The units of q_A are, $\frac{\text{gm. moles F.R. per kgm. sample}}{\% \text{ Species A}}$)

$$q_{S119} = \frac{(1.1 \times 10^{16} \times 10^3)/6.02 \times 10^{23}}{100} = 1.83 \times 10^{-7} \quad 44.$$

$$q_{S120} = \frac{(4.4 \times 10^{16} \times 10^3)/6.02 \times 10^{23}}{100} = 7.31 \times 10^{-7} \quad 45.$$

$$q_{S61-6} = \frac{(5.7 \times 10^{16} \times 10^3)/6.02 \times 10^{23}}{100} = 9.47 \times 10^{-7} \quad 46.$$

$$q_{S61-9} = \frac{(11 \times 10^{16} \times 10^3)/6.02 \times 10^{23}}{100} = 18.3 \times 10^{-7} \quad 47.$$

V. RESULTS

A. Introduction

All of the polymerizations made in this study have been conducted in the Aminco autoclave described in the experimental section. This study has been principally concerned with the manner in which asphalt systems are capable of interacting in reactions with vinyl monomers. Vinylbenzene has been the monomer used in the major part of this study. Other monomers used were α -vinyl naphthalene and vinyl-2-ethylhexanoate. Several typical petroleum residua, representing a wide range of types normally encountered, were the asphalt material used in this study. The properties of these asphalts were given in Table 4, page 33.

The Gulf Coast naphthenic residuum, S 119, and the East Central Texas residuum, S 120, which represent residua of low and high asphaltene content, respectively, have been studied extensively. Polymerizations have also been made in which the asphaltene removed from these asphalts by n-pentane precipitation were used. It will be shown subsequently that the asphaltene fraction of these asphalts contains the majority of the ingredients which are the key to the phenomena observed herein.

Included in these results is the manner in which the polymerization rates of the systems studied may be correlated empirically with the variables, monomer concentration and reaction temperature.

The nature of this work is such that a considerable amount of experimental effort was required to conduct a single polymerization

run. This run yields a set of data from which may be obtained a single value, namely K , the overall polymerization rate constant. With this single value, if the initial concentrations are known, it is possible to again construct the entire curve representing the results of this run. Therefore, the quantity of data cited in this section may appear to be small. The numerical values of these empirically determined rate constants are tabulated at the end of this section. The original raw data from the polymerization experiments are given in the appendix.

B. Correlation of Polymerization Rates With Monomer Concentration

Experimental data are obtained in a tabulated form with the unreacted monomer concentration (weight percent) measured as a function of the time elapsed (minutes) from the start of polymerization. It has been found that straight lines are obtained if these data are plotted with reciprocal monomer concentration (weight percent)⁻¹ as ordinate, versus the time elapsed (minutes) from the start of polymerization as abscissa. Figures 10 and 11 included in this section, and Figure 9 of the calculation section and Figure 7 of the experimental section have been plotted in this manner. The straight line dependence as shown in these figures is typical of the data obtained in all of the polymerizations performed.

This type of data may be correlated by means of a second order rate equation in terms of monomer concentration. (Refer to the calculations section.) This equation follows:

$$-d(M)/dT = K(M)^2$$

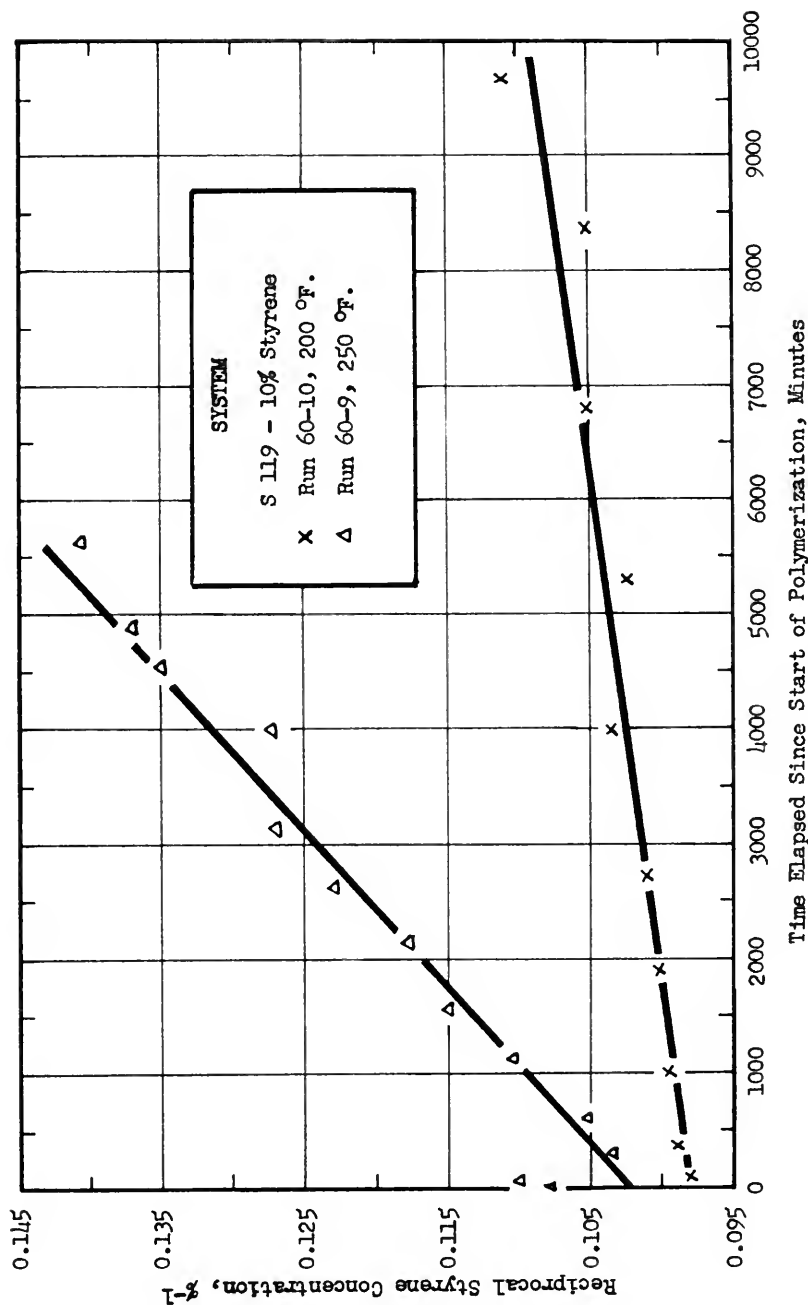


Figure 10, The effect of temperature on the rate of polymerization.

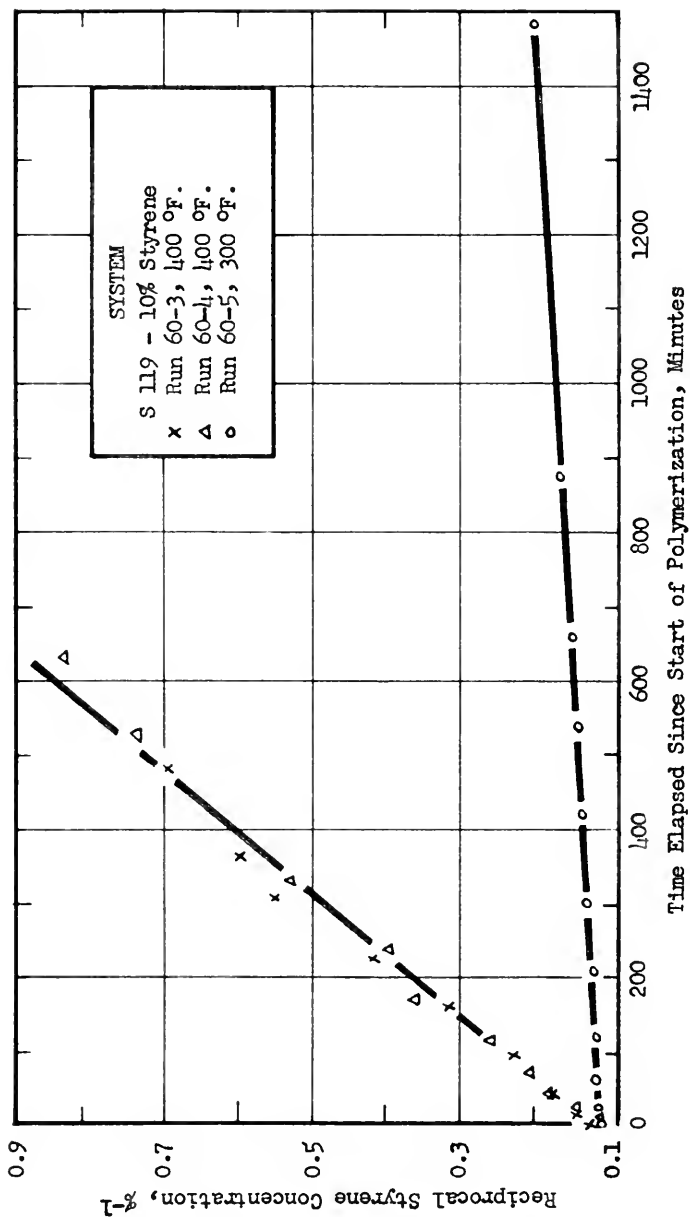


Figure 11, The effect of temperature on the rate of polymerization.

If the units are applied consistently and the data plotted as just mentioned, K will be identically equal to the slope of the line obtained and have the units, $(\text{min.})^{-1}(\text{percent monomer})^{-1}$. Here K has been used as the empirically determined overall polymerization rate constant.

Check runs on the same systems under the same conditions have agreed within about 10 percent. Data from the runs which have been made in duplicate in this study are presented in Table 9.

TABLE 9, A COMPARISON OF EXPERIMENTALLY DETERMINED RATE
CONSTANTS TO SHOW REPRODUCIBILITY

Polymerization Run Conditions: These runs were charged with the percent asphalt as indicated below plus a quantity of Styrene approaching 10% with xylene comprising the difference.

Run No.	Asphalt	% Asphalt	Temperature, °F.	Overall Rate Constant, $\text{min.}^{-1} \times \%$
R61-4	none	-- -	300	4.08×10^{-5}
R61-5	none	-- -	300	4.12×10^{-5}
R61-16	none	-- -	300	3.96×10^{-5}
R60-19	S 120	90.0	300	10.85×10^{-5}
R60-22	S 120	90.0	300	10.09×10^{-5}
R60-4	S 119	90.0	400	1.17×10^{-3}
R60-3	S 119	90.0	400	1.22×10^{-3}

The effect of precipitation of the polymer during the polymerizations has been recognized as a possible source of erroneous results.

Petrolatum, a solvent incompatible with the polystyrene, was used to determine the magnitude of this effect. The rate constant determined for this run is plotted in Figure 12 for the purpose of comparison with the data obtained for asphalt systems. It is obvious that the possible source of error is potentially quite large. The possible occurrence of a polymer precipitate on the interior of the autoclave would be readily observable. This did not ever occur, however, for polymerization in any of the other solvent systems used.

C. The Arrhenius Correlation

It is apparent from the data given in Figures 10 and 11 that temperature is a very important variable. This is in accordance with the effect observed for many reaction systems that are essentially irreversible. As might be expected from the work of others in the polymer field, it has been possible to correlate this temperature dependence by means of the Arrhenius equation. The same data shown in Figures 10 and 11, for the Gulf Coast naphthenic residuum (S 119) have been used to calculate the overall polymerization rate constant, K, and plotted in Figure 12. The second line shown in this figure is for the air-blown asphalt R60-11.

The slopes of these lines are about $-8,060^{\circ}\text{R}$.

The energy of activation, H, is therefore,

$$H = -1.104 (-8,060)/0.4343 = +20,500 \text{ cal. per gm. mole} \quad 49.$$

If a 1.0 percent positive correction is applied, as estimated in the calculation section, H will be for these systems:

$$H = 1.01 (20,500) = 20,700 \text{ cal. per gm. mole.} \quad 50.$$

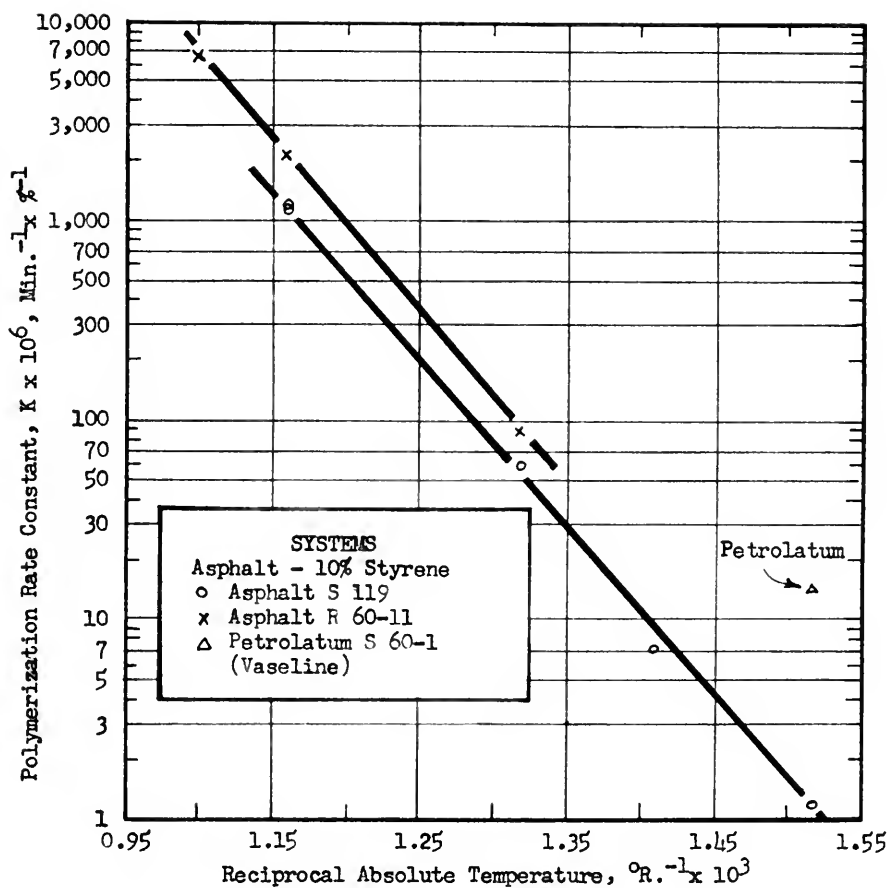


Figure 12, Arrhenius temperature correlation of overall polymerization rate constants.

Bamford and Barb, in their review of polymerization processes, cite values of H , the activation energy of the thermal polymerization constant of styrene ranging from 19,200 to 23,200 cal. per gm. mole.⁽¹⁴⁾ These values were determined over the temperature range of 0 to 120 °C., which is somewhat lower than the temperature range of this study. It may be noted that the value of H obtained here is within the range determined by other investigators.

Although the data obtained are insufficient to allow an accurate calculation of the activation energies (only one or two points obtained per system), the data of Figure 13 show qualitative agreement with those obtained for the more definitive data presented in Figure 12.

D. Asphaltene Constituents Exhibit a Dominant Effect

Data have been obtained to show that components concentrated in the asphaltene fraction are largely responsible for the influence that the asphalts studied have had on the polymer kinetics. Reference to Figure 13 indicates that asphalts having a high asphaltene content have caused the greatest acceleration of the polymerization rate. At a reciprocal temperature corresponding to 300 °F., the rate constant obtained for polymerization in xylene is shown for comparison. This single point represents the results of three runs made on the separate batches of styrene used in the runs with the asphalt systems. The "A" group of asphalts has 20-40 percent asphaltenes while the "B" group has only 1.5-2.6 percent asphaltenes.

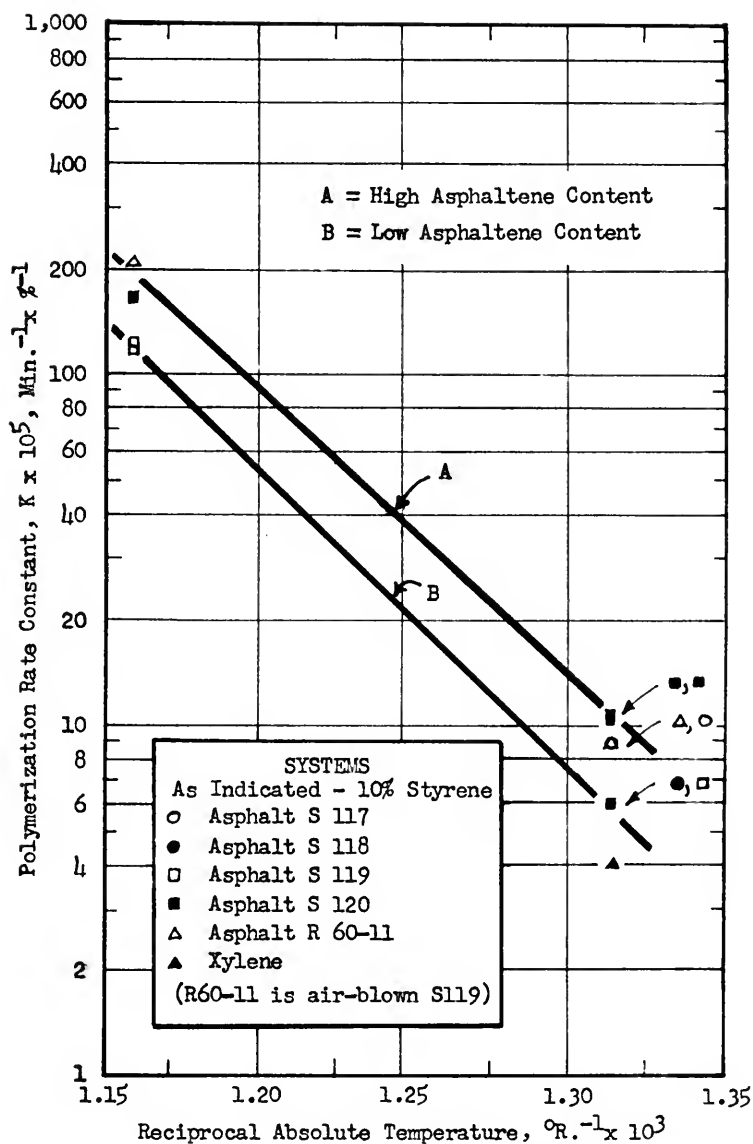


Figure 13, Summary of the overall polymerization rate constants obtained in the various systems studied.

It is obvious that the grouping of these data in this manner is permissible; however, it must also be noted that the sulfur content (see Table 4, page 33) of the asphalts has a similar relationship.

The asphalt S 119, having a low asphaltene content, and the asphalt S 120, having a high asphaltene content, were selected for further investigation of the asphaltene content variable. By concentration of the asphaltenes in one fraction through n-pentane precipitation, and removal from the remaining asphalt by filtration, it was possible to study the two fractions separately. If asphaltene concentration is an important variable, it should be possible to observe its effect by dilution of the asphaltene with a suitable inert solvent, or solvent having known effects. Xylene was chosen because it is mutually compatible with styrene, asphaltenes and polymer, and is known to have no acceleration influence of its own. The results of these experiments are shown in Figure 14. It can be seen that at low asphaltene concentrations, acceleration of the polymerization is pronounced. As the concentration is increased, this acceleration gradually disappears. Also, it can be seen that differences in the character of the asphaltenes themselves have a noticeable effect on the rate, since the asphaltenes from S 120 gave a substantially greater acceleration than did the asphaltenes from S 119.

Repeating these experiments with the base asphalts S 119 and S 120 yields results analogous to those obtained for the asphaltenes. These results are shown in Figure 15. An important difference should

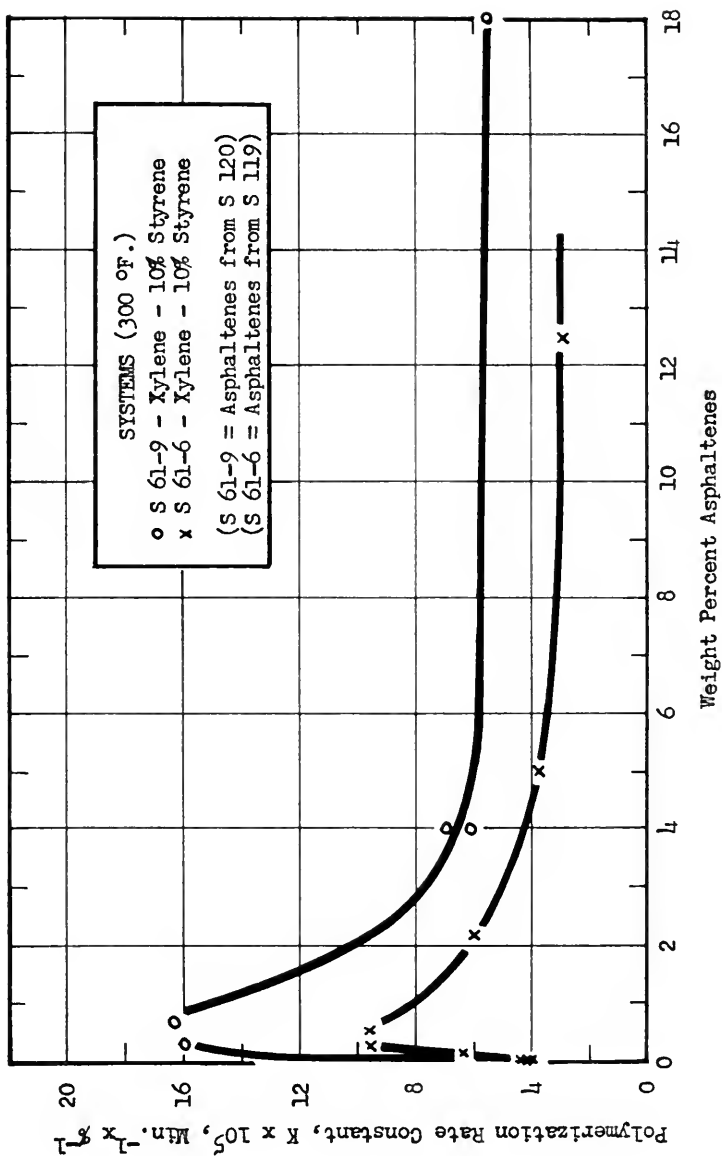


Figure 11, The effect of variation in asphaltene concentration on the polymerization rate constant.

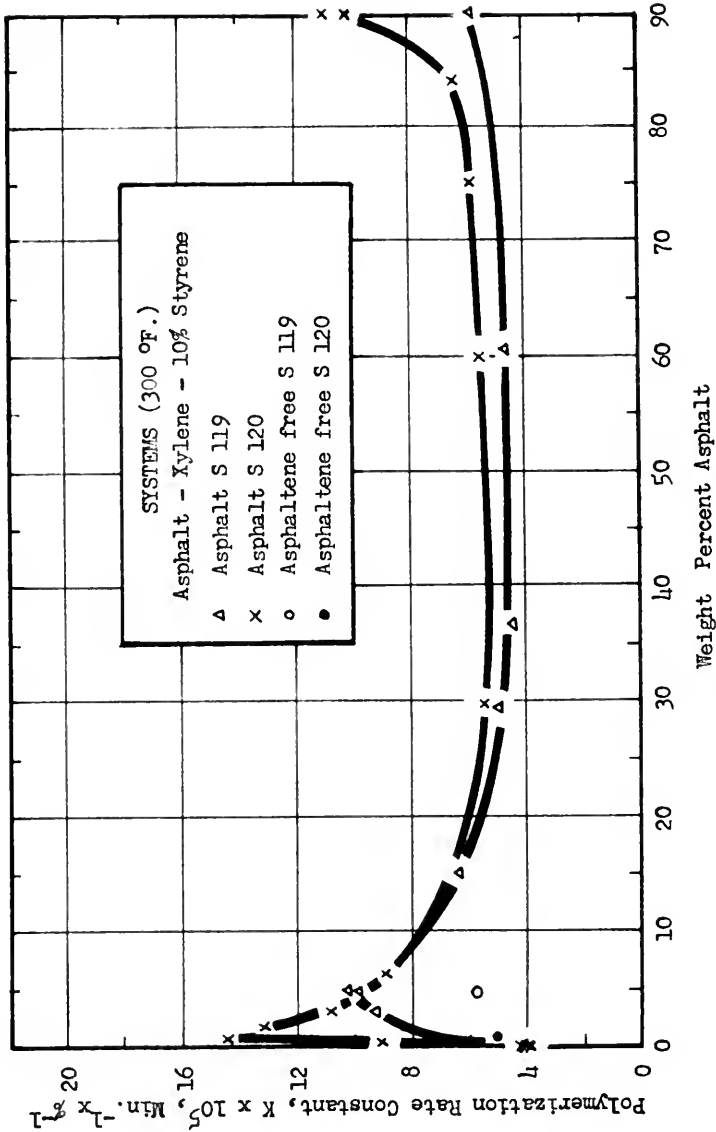


Figure 15, The effect of variation in asphalt concentration on the polymerization rate constant.

be noted for these plots since the concentration variable is extended considerably in Figure 15. These data indicate the diluting effect of the inert asphalt fractions. Polymerizations at the concentration of asphalt yielding the maximum rates, were made, using the asphaltene free residues (containing less than 0.3 wt. percent). The results of these polymerization runs are shown in Figure 15. The acceleration of polymerization noted for the original asphalts, at the concentration of asphalt yielding the maximum rates, was greatly reduced. This strongly demonstrates that the asphaltene fraction and constituents contained therein are a key factor of this phenomenon.

Mention should be made of phenomena which are manifest for the asphalt systems, not observed for studies of the asphaltene fractions. As relatively high asphalt concentrations are reached, the polymerization is again accelerated. Clarification of the cause of this will be covered in the discussion of results.

Earlier in this section it was noted that asphalts with high asphaltene content had the greatest acceleration influence. Among this group was the air-blown asphalt R60-11, prepared from S 119. In Figure 16, the concentration variable for S 119 and R60-11 is compared. The acceleration obtained for the air-blown asphalt is not particularly diminished by increasing asphalt concentration, as is the case for the residuum S 119.

Although it has not been explicitly stated, styrene has been the only monomer for which results have been cited up to this point. In order to generalize this study, other monomers were included.

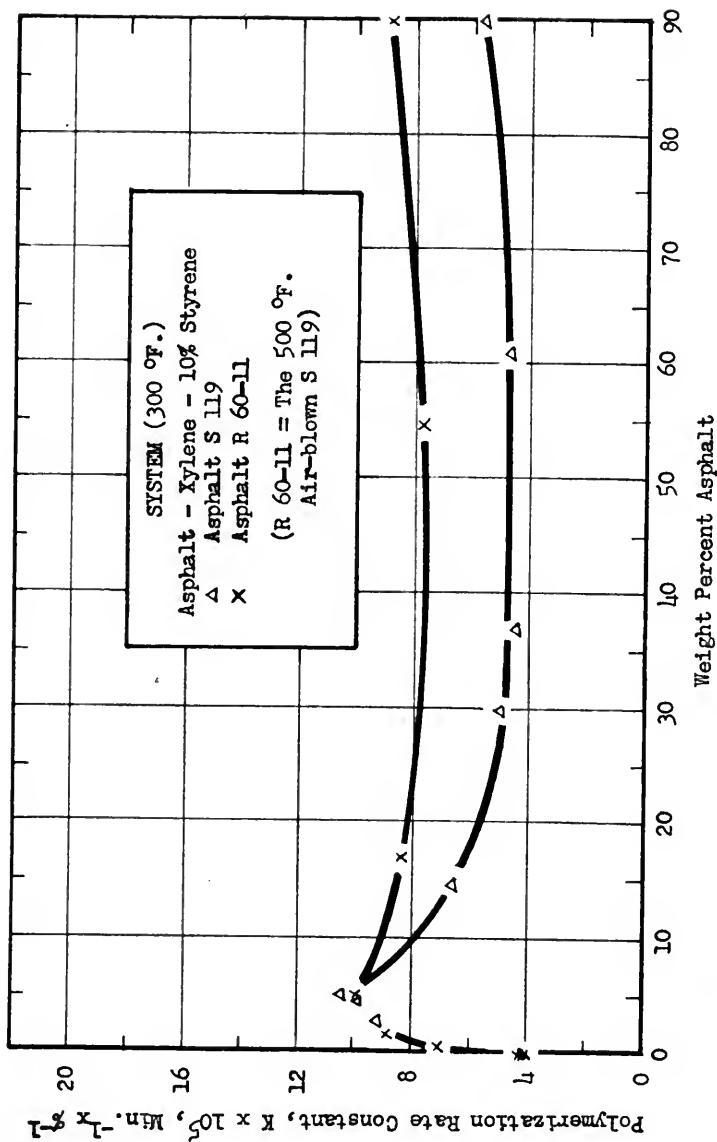


Figure 16, A comparison of the influence of an air-blown asphalt with that of the residuum from which it was prepared.

Alpha-vinylnaphthalene and vinyl-2-ethylhexanoate were polymerized in xylene and in xylene containing asphaltenes obtained from the asphalt S 120. Vinyl-2-ethylhexanoate which had no measurable thermal polymerization of its own was not caused to polymerize by the addition of the asphaltene. The presence of asphaltenes did affect the polymerization rate of α -vinylnaphthalene.

Since no polymerization occurred for vinyl-2-ethylhexanoate, the data obtained are not included. A control test containing one percent benzoyl peroxide in this monomer caused gelling to occur at 200 °F. in 2.5 hours.

The data obtained for α -vinylnaphthalene is plotted in Figure 17. Because very few points were obtained for this system, the curve drawn has been made dashed. Data were limited because of the high cost of this compound. There is qualitative agreement of these data with those obtained for the styrene systems. The magnitude of the observed effect is not large, being of the order of the anticipated experimental error for these polymerization experiments.

E. Influence of a Pure Stable Free Radical

Stabilized free radicals were suspected of being the constituent present in the asphaltene fraction which is responsible for the phenomena observed. Experiments using 1,1-diphenyl-2-picrylhydrazyl yielded the results plotted in Figure 18. Although the data are somewhat scattered, there is at least an indication of an acceleration effect followed by a gradual decrease of this effect as the free radical concentration is increased. It is believed that the

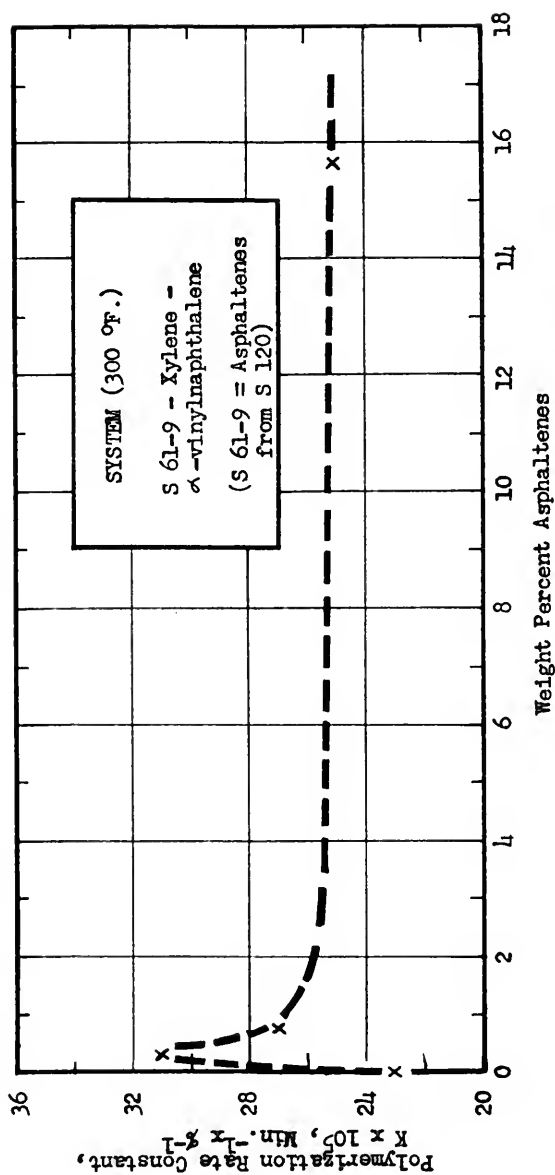


Figure 17, The effect of variation in asphaltene concentration on the polymerization rate constant.

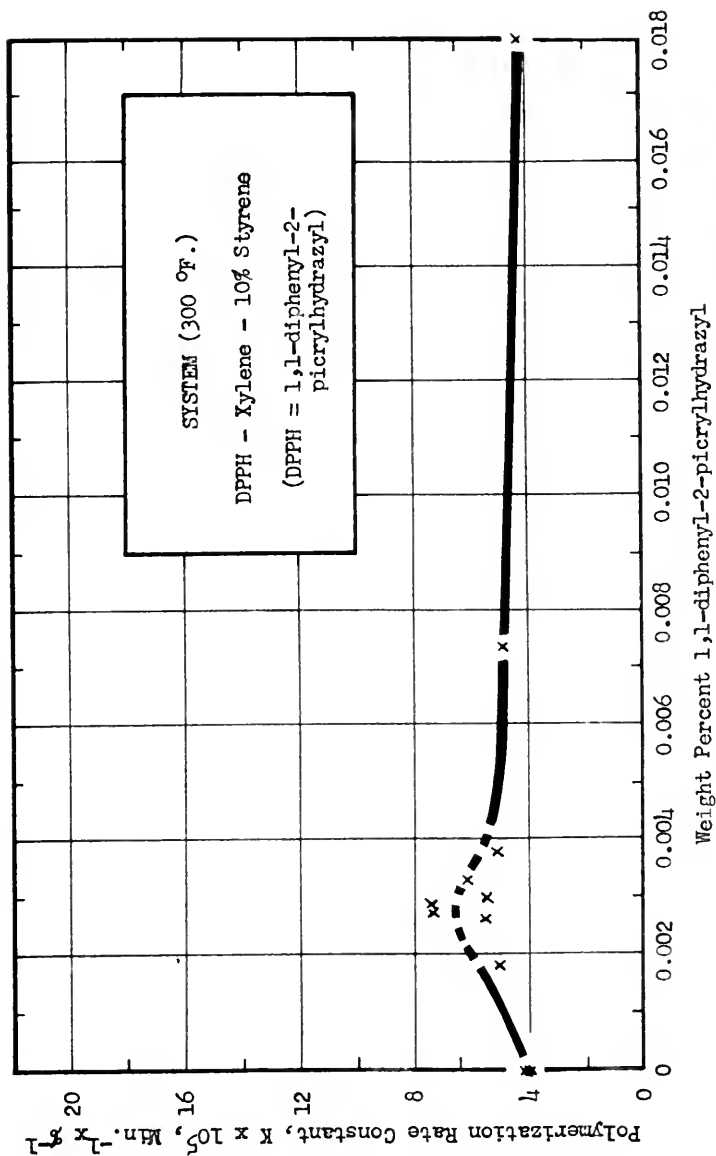


Figure 18, The effect of variation in the concentration of a pure free radical on the polymerization rate constant.

acceleration noted here is definite, based on the reproducibility of the experiments conducted in pure xylene. The spread in the values obtained at the maximum is probably caused by the delicate balance of factors responsible for the occurrence of this maximum acceleration.

F. Spectroscopic Evidence of The Existence
of Stable Free Radicals

The four asphalts used in this study, and the two asphaltenes prepared from these asphalts were submitted for analysis by ESR, on a contract basis, to the:

Ridgefield Instrument Group
Schlumberger Corporation
P. O. Box 337
Ridgefield, Connecticut

The determinations were made on a relative basis by comparison at the same instrument gain. Examination was made at a field-strength of 3,380 gauss, with a micro-wave frequency of 9.47 kilomegacycles. The spectroscopic splitting factor, "g", was determined to be 2.0021 for these materials. This is quite close to the theoretical value which can be calculated for the free-electron, i.e., 2.0023.(52)

TABLE 10, FREE RADICAL CONCENTRATION OF THE ASPHALTS
AND ASPHALTENES USED IN THIS STUDY

Sample	(a) Calculated Relative Signal (Instrument Value/gm.)	(b) Concentration Free Radicals/gm.
<hr/>		
Asphalts		
S 117	597	5.1×10^{16}
S 118	55	0.47×10^{16}
S 119	123	1.1×10^{16}
S 120	510	4.4×10^{16}
Asphaltenes		
S 61-6	660	5.7×10^{16}
S 61-9	1281	11×10^{16}
<hr/>		

- (a) These values are estimated to be accurate to within about 10 percent of the value determined. They are the average of determinations made in duplicate.
- (b) Determined by comparison with a 0.002 M aqueous solution of MnCl_2 .
- (c) Measurements were made by Schlumberger Corporation using a Strand Labs Model No. 600 spectrometer at 9.47 kmc. and 3380 gauss. Samples were prepared by means of scooping 1.5 mm. diameter pyrex capillary tubes.

TABLE 11, GRAPHICALLY DETERMINED OVERALL POLYMERIZATION RATE CONSTANT FOR RUNS WITH THE GULF COAST NAPHTHENIC RESIDUUM (S119), STYRENE AND XYLENE

Polymerization Run Conditions: These runs were charged with the percent S119 as indicated below, plus a quantity of Styrene approaching 10%, with Xylene comprising the difference.

Run No.	% S119	Temperature, °F.	Overall Rate Constant (min. ⁻¹ x % ⁻¹)
R61- 4	0.0	300	4.08 x 10 ⁻⁵
R61- 5	0.0	300	4.12 x 10 ⁻⁵
R61-16	0.0	300	3.96 x 10 ⁻⁵
R61-48	2.91	300	9.32 x 10 ⁻⁵
R61- 3	4.97	300	9.92 x 10 ⁻⁵
R61- 6	4.99	300	10.57 x 10 ⁻⁵
R61- 7	14.9	300	6.54 x 10 ⁻⁵
R61- 2	29.8	300	5.00 x 10 ⁻⁵
R61- 8	36.9	300	4.38 x 10 ⁻⁵
R61- 1	60.6	300	4.75 x 10 ⁻⁵
R60- 5	90.0	300	5.87 x 10 ⁻⁵
R60-10	89.2	200	1.07 x 10 ⁻⁶
R60- 9	89.8	250	7.22 x 10 ⁻⁶
R60- 4	90.0	400	1.17 x 10 ⁻³
R60- 3	90.0	400	1.22 x 10 ⁻³

The following run was made with S119 after removal of asphaltenes by precipitation with n-pentane. This material designated S61-1.

Run No.	% S61-1	Temperature, °F.	Overall Rate, Constant (min. ⁻¹ x % ⁻¹)
R61- 9	4.83	300	5.79 x 10 ⁻⁵

TABLE 12, GRAPHICALLY DETERMINED OVERALL POLYMERIZATION RATE CONSTANT FOR RUNS WITH THE EAST CENTRAL TEXAS RESIDUUM (S120), STYRENE AND XYLENE

Polymerization Run Conditions: These runs were charged with the percent S120 as indicated below, plus a quantity of Styrene approaching 10%, with Xylene comprising the difference.

Run No.	% S120	Temperature, °F.	Overall Rate Constant (min. ⁻¹ x % ⁻¹)
R61- 4	0.0	300	4.08 x 10 ⁻⁵
R61- 5	0.0	300	4.12 x 10 ⁻⁵
R61-16	0.0	300	3.96 x 10 ⁻⁵
R61-24	0.266	300	9.14 x 10 ⁻⁵
R61-23	0.839	300	15.4 x 10 ⁻⁵
R61-22	1.63	300	13.05 x 10 ⁻⁵
R61-18	3.21	300	10.78 x 10 ⁻⁵
R61-17	6.39	300	8.92 x 10 ⁻⁵
R61-31	29.9	300	5.32 x 10 ⁻⁵
R61-32	60.0	300	5.56 x 10 ⁻⁵
R61-33	75.3	300	5.83 x 10 ⁻⁵
R61-35	84.2	300	8.33 x 10 ⁻⁵
R60-19	90.0	300	10.85 x 10 ⁻⁵
R60-22	90.0	300	10.09 x 10 ⁻⁵
R60-21	90.0	400	1.65 x 10 ⁻³

The following run was made with S120 after removal of asphaltenes by precipitation with n-pentane. This material designated S61-12.

Run No.	% S61-12	Temperature, °F.	Overall Rate, Constant (min. ⁻¹ x % ⁻¹)
R61-40	0.837	300	4.96 x 10 ⁻⁵

TABLE 13, GRAPHICALLY DETERMINED OVERALL POLYMERIZATION RATE CONSTANT FOR RUNS WITH 500°F AIR BLOWN S119 (R60-11), STYRENE AND XYLENE

Polymerization Run Conditions: These runs were charged with the percent R60-11 as indicated below, plus a quantity of Styrene approaching 10%, with Xylene comprising the difference.

<u>Run Number</u>	<u>R60-11</u>	<u>Temperature, °F.</u>	<u>Overall Rate Constant (min.⁻¹ x %⁻¹)</u>
R61-4	0.0	300	4.08 x 10 ⁻⁵
R61-5	0.0	300	4.12 x 10 ⁻⁵
R61-16	0.0	300	3.96 x 10 ⁻⁵
R61-45	0.573	300	7.06 x 10 ⁻⁵
R61-46	1.57	300	8.85 x 10 ⁻⁵
R61-47	5.02	300	9.93 x 10 ⁻⁵
R61-49	17.0	300	8.35 x 10 ⁻⁵
R61-54	54.8	300	7.73 x 10 ⁻⁵
R60-13	89.9	300	8.82 x 10 ⁻⁵
R60-12	89.9	400	2.13 x 10 ⁻³
R60-14	90.1	450	6.55 x 10 ⁻³

TABLE 14, GRAPHICALLY DETERMINED OVERALL POLYMERIZATION RATE CONSTANT
FOR RUNS WITH VARIOUS PETROLEUM MATERIALS

Polymerization Run Conditions: These runs were charged with the material as indicated below, plus a quantity of Styrene approaching 10%.

<u>Run Number</u>	<u>Material</u>	<u>Temperature, °F.</u>	<u>Overall Rate Constant (min.⁻¹ x %⁻¹)</u>
R60-15(a)	S60-1 (S60-1 is petrolatum)	200°	1.49 x 10 ⁻⁵
R60-20	S117 (S117 is the East Texas Asphalt Base Residuum)	300°	8.86 x 10 ⁻⁵
R60-18	S118 (S118 is the South Texas Heavy Asphalt Base Residuum)	300°	5.88 x 10 ⁻⁵

(a) A definite precipitation of polymer occurred on the interior of the autoclave during this run.

TABLE 15, GRAPHICALLY DETERMINED OVERALL POLYMERIZATION RATE CONSTANT FOR RUNS WITH ASPHALTENES DERIVED FROM S119 THE GULF COAST NAPHTHENIC RESIDUUM (S61-6), STYRENE AND XYLENE

Polymerization Run Conditions: These runs were charged with the percent S61-6 as indicated below, plus a quantity of Styrene approaching 10%, with Xylene comprising the difference.

Run No.	% S61-6	Temperature, °F.	Overall Rate Constant (min. ⁻¹ x % ⁻¹)
R61- 4	0.0	300	4.08 x 10 ⁻⁵
R61- 5	0.0	300	4.12 x 10 ⁻⁵
R61-16	0.0	300	3.96 x 10 ⁻⁵
R61-15	0.101	300	6.33 x 10 ⁻⁵
R61-14	0.250	300	9.48 x 10 ⁻⁵
R61-11	0.502	300	9.53 x 10 ⁻⁵
R61-12	1.00	300	9.10 x 10 ⁻⁵
R61-13	2.19	300	5.93 x 10 ⁻⁵
R61-10	4.97	300	3.70 x 10 ⁻⁵
R61-36	12.9	300	2.81 x 10 ⁻⁵

TABLE 16, GRAPHICALLY DETERMINED OVERALL POLYMERIZATION RATE CONSTANT FOR RUNS WITH ASPHALTENES DERIVED FROM S120 THE EAST CENTRAL TEXAS RESIDUUM (S61-9), STYRENE AND XYLENE

Polymerization Run Conditions: These runs were charged with the percent S61-9 as indicated below, plus a quantity of Styrene approaching 10%, with Xylene comprising the difference.

Run No.	% S61-9	Temperature, °F.	Overall Rate. Constant (min. ⁻¹ x % ⁻¹)
R61- 4	0.0	300	4.08×10^{-5}
R61- 5	0.0	300	4.12×10^{-5}
R61-16	0.0	300	3.96×10^{-5}
R61-38	0.268	300	15.9×10^{-5}
R61-37	0.653	300	16.3×10^{-5}
R61-34	4.02	300	6.04×10^{-5}
R61-35	4.01	300	6.92×10^{-5}
R61-39	18.1	300	5.42×10^{-5}

TABLE 17, GRAPHICALLY DETERMINED OVERALL POLYMERIZATION RATE CONSTANT FOR RUNS WITH ASPHALTENES DERIVED FROM S120 THE EAST CENTRAL TEXAS RESIDUUM (S61-9), α -VINYLNAPHTHALENE AND XYLENE

Polymerization Run Conditions: These runs were charged with the percent S61-9 as indicated below, plus a quantity of α -vinyl-naphthalene approaching 13.5%, with Xylene comprising the difference.

Run No.	% S61-9	Temperature, °F.	Overall Rate Constant (min. ⁻¹ x % ⁻¹)
R61-50	0.0	300	23 x 10 ⁻⁵
R61-51	0.299	300	31 x 10 ⁻⁵
R61-52	0.745	300	27 x 10 ⁻⁵
R61-53	15.7	300	25 x 10 ⁻⁵

TABLE 18, GRAPHICALLY DETERMINED OVERALL POLYMERIZATION RATE CONSTANT FOR RUNS WITH 1,1-DIPHENYL-2-PICRYLHYDRAZYL (S61-11), STYRENE AND XYLENE

Polymerization Run Conditions: These runs were charged with the percent S61-11 as indicated below, plus a quantity of Styrene approaching 10%, with Xylene comprising the difference.

Run No.	% S61-11	Temperature, °F.	Overall Rate Constant (min. ⁻¹ x % ⁻¹)
R61- 4	0.0	300	4.08 x 10 ⁻⁵
R61- 5	0.0	300	4.12 x 10 ⁻⁵
R61-16	0.0	300	3.96 x 10 ⁻⁵
R61-19	0.0018	300	4.96 x 10 ⁻⁵
R61-29	0.0026	300	5.52 x 10 ⁻⁵
R61-25	0.0028	300	7.00 x 10 ⁻⁵
R61-26	0.0029	300	7.17 x 10 ⁻⁵
R61-27	0.0030	300	5.40 x 10 ⁻⁵
R61-30	0.0033	300	6.12 x 10 ⁻⁵
R61-21	0.0038	300	5.40 x 10 ⁻⁵
R61-28	0.0074	300	4.88 x 10 ⁻⁵
R61-20	0.018	300	4.39 x 10 ⁻⁵

VI. DISCUSSION OF RESULTS

A. Introduction

In the preceding pages reference to the literature and experimentally determined facts has been used to establish a background for the following explanations of the phenomena that have been observed. In review, it has been shown that stabilized free radicals can exist in nature and do occur in petroleum materials, particularly the high molecular weight colloidal portions of crudes and the asphaltene fraction of asphalts. More specifically, they have been demonstrated to be present in the asphalts studied by direct measurement, using ESR techniques. In addition to the existence of these free radicals, the catalytic influence of materials which are known to contain stabilized free radicals has been shown by the work presented herein, and reference has been made to similar phenomena observed by other investigators.

B. The Theoretical Kinetic Equation

An equation has been developed from theoretical considerations of vinyl-polymerization processes to correlate the kinetic variables of monomer and stabilized free radical concentration. This equation is as follows:

$$-d(M)/dT = K(M)^2 \quad 51.$$

Where: K Denotes the empirically determined overall polymerization rate constant or the theoretically calculated overall polymerization rate constant, (min.)⁻¹(percent)⁻¹

In the theoretical development of this equation it has been shown, assuming the theory to be correct, that (see pages 64 and 65),

$$K = A \left[(R_S^2 + BR_S^D + C)^{\frac{1}{2}} - R_S \right] \quad 52.$$

A, B and C are constants which result from a grouping of the individual reaction step rate constants. The constant D is introduced to represent a simple non-linear function which has theoretical significance, in that all of the non-idealities of the reaction system are "lumped" into this one constant. The substitution of the parameters to determine A, B, C, etc. is shown in the calculation section. Here the term ideality is taken to mean that the rate of reactions, as written for the mechanism postulated, follows the rate equations indicated with strict proportionality.

It is believed that a comparison of the experimental results with those calculated utilizing this theoretical equation will confirm the hypothesis that the stabilized free radicals present in asphalts and possibly other natural materials, actually can interact in a catalytic fashion with polymer systems, in particular those resulting from styrene polymerization. Before this comparison is made, however, the analytic properties of this equation itself shall be discussed.

Analysis of the Theoretical Kinetic Equation Related to Monomer Concentration

When the stabilized free radical concentration is held constant, K. is constant. This rate equation then becomes a simple second order rate equation. It should, therefore, be possible to obtain a straight

line by plotting reciprocal monomer concentration versus time for a given polymerization experiment if the system remains homogeneous and the temperature is held constant.

Analysis of the Theoretical Kinetic Equation Related to Stable Free Radical Concentration

By examining the properties of K which is simply multiplied by the square of the monomer concentration to obtain the instantaneous rate, the effect on rate may be seen. The value of K may be looked upon as a result of two basic factors. These factors are the accelerating influence of the stabilized free radicals in the capacity of starting new polymer chains, and the ability of them to cause chain termination to increase at a greater rate. These two effects may be seen analytically as follows:

$$K = A \left[(R_s^{2*} + BR_s^{D*} + C)^{\frac{1}{2}} - R_s^* \right] \quad 53.$$

$$B = 4k_{ta} k_s / k_{ts}^2 \quad 54.$$

$$C = 8k_{ta} k_c / k_{ts}^2 \quad 55.$$

When the self-initiation by a monomer may be considered not to occur, i.e., when k_c is zero, C is zero. If D lies between 1.0 and 0, the result is that,

$$K = A \left[(R_s^{2*} + BR_s^{D*})^{\frac{1}{2}} - R_s^* \right] \quad 56.$$

Taking the derivative of K with respect to R_s^* yields,

$$\frac{dK}{dR_s^*} = A \left[\frac{2R_s^* + DBR_s^{(D-1)*}}{2(R_s^{2*} + BR_s^{D*})^{\frac{1}{2}}} - 1 \right] \quad 57.$$

When R_s^* is zero, the slope is $+\infty$. As R_s^* becomes increasingly large the slope approaches zero through positive values. The curve

obtained, therefore, has the general characteristics as shown in Figure 19(a). This can be interpreted as the effect caused by the initiation of growing polymer chains by the stabilized free radicals.

If polymerization initiation by stabilized free radicals may be considered not to occur, even though chain termination does

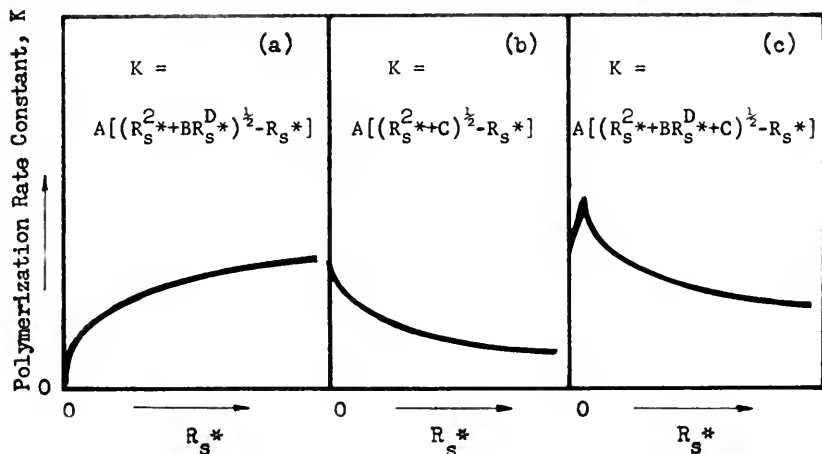


Figure 19, Qualitative aspects of the factors affecting the overall polymerization rate constant.

continue to occur, k_s and B will be zero. The result is that,

$$K = A \left[(R_S^{2*} + C)^{1/2} - R_S^* \right] \quad 58.$$

Taking the derivative of K with respect to R_S^* gives,

$$\frac{dK}{dR_S^*} = A \left[\frac{R_S^*}{(R_S^{2*} + C)^{1/2}} - 1 \right] \quad 59.$$

When R_S^* is zero, the slope of the curve is $-A$. As R_S^* becomes larger, the slope approaches zero always through negative values. The curve obtained, therefore, has the general characteristics as

shown in Figure 19(b). This illustrates the termination effect of stabilized free radicals in the kinetic process.

When neither k_c nor k_s is zero, and D lies between 1.0 and 0.0, the result of these two competing effects is that K varies in the manner illustrated in Figure 19(c). When $D = 1.0$, a special case arises for the general equation. It can be shown by taking the derivative that neither a maximum nor a minimum will occur except when the situation arises that, $B = 2C^{\frac{1}{2}}$, in which case K has a constant value equal to,

$$\begin{aligned} K &= A \left[(R_s^2 + 2C^{\frac{1}{2}}R_s + C)^{\frac{1}{2}} - R_s \right] \\ &= A \left[((R_s + C^{\frac{1}{2}})^2)^{\frac{1}{2}} - R_s \right] \\ &= AC^{\frac{1}{2}} \end{aligned}$$

60.

In the preceding discussion the analytical properties of the equation that has been derived have been presented. The manner in which a maximum value for K is attained should, therefore, be clear. At this point, it is convenient to mention that this maximum is analytically a direct result of introducing the exponent D into the equation. However, in the actual formulation of the theory, no particular justification has been given for this mathematical manipulation.

Further study of the functional relationships of the various parameters of the equation developed for K will show that any manipulation which has the effect of shifting the curve shown in Figure 19(a) to the left with respect to the curve shown in Figure 19(b),

will yield a result similar to that developed for the curve shown in Figure 19(c). A point that should be brought out here, is that the theoretical derivation under consideration has involved the use of some fairly extensive assumptions. The equation which has been derived for the rate constant is a function which is delicately poised, i.e., the maximum value for K is attained through the subtle effects discussed. It is, therefore, quite conceivable that slight variations from the assumptions made in this derivation can cause the required shift just presented. It is for this reason that the use of the exponent D, which has exactly this type of capability, is believed justified. It is recognized that this is not a completely rigorous development.

C. A Comparison of Theory with Experiment; Correlation of Polymerization Rates with Monomer Concentration

A second order dependence of the rate on the monomer concentration has been predicted from theoretical considerations. This has been confirmed to hold true during all of the experiments of this investigation. The monomer concentration in the reaction systems has been varied from 1 to 10 percent. The range of temperature has been 200 °F. to 450 °F. Thus, it has been possible to correlate all of the polymerization data obtained by means of a second order rate constant.

Stabilized Free Radicals Influence Vinyl Polymerization

Polymerization rates which have been determined have been correlated through use of the polymerization rate constant, K. It is, therefore, more convenient to discuss factors that influence the

value of K than those affecting the instantaneous rates. Experimental results have shown K to be influenced by constituents that are concentrated in the asphaltene fraction of the asphalts used and by the stabilized free radical DPPH. The concentration of stabilized free radicals in the asphaltene fraction of S 120 is 2.5 times that of the concentration in the asphalt, S 120. The concentration of stabilized free radicals in the asphaltene fraction of S 119 is 5.4 times that of the concentration in the asphalt, S 119. This evidence certainly indicates that the stabilized free radicals may be responsible for the phenomena observed.

The data originally plotted in Figures 14 and 15, with the abscissa expressed in weight percent asphalt or asphaltene present, have been converted to a scale that is estimated to be the concentration of free radicals present in the system, and plotted in Figure 20. This has been achieved by utilizing the assumption that the free radical concentration is proportional to the asphalt or asphaltene concentration expressed in weight percent and the relative concentrations of free radicals that have been determined for these materials. The details of this have been shown in the calculation section. Included in Figure 20 are curves calculated from the theoretical equation for K. These data are for styrene systems only. The data obtained for the α -vinylnaphthalene system has been treated similarly. The result is shown in Figure 21.

The agreement of the calculated values with the experimental values is apparent. It has been possible to obtain this close agreement of the mathematical model with experimental data by

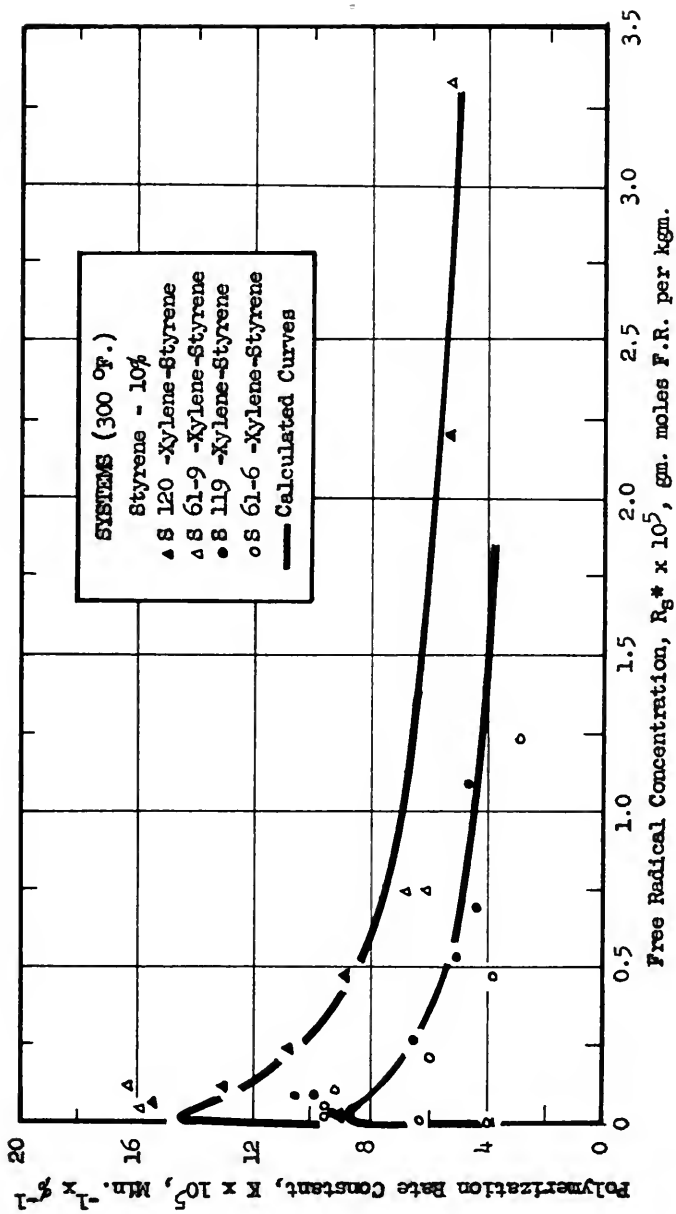


Figure 20, A comparison of theory with experiment.

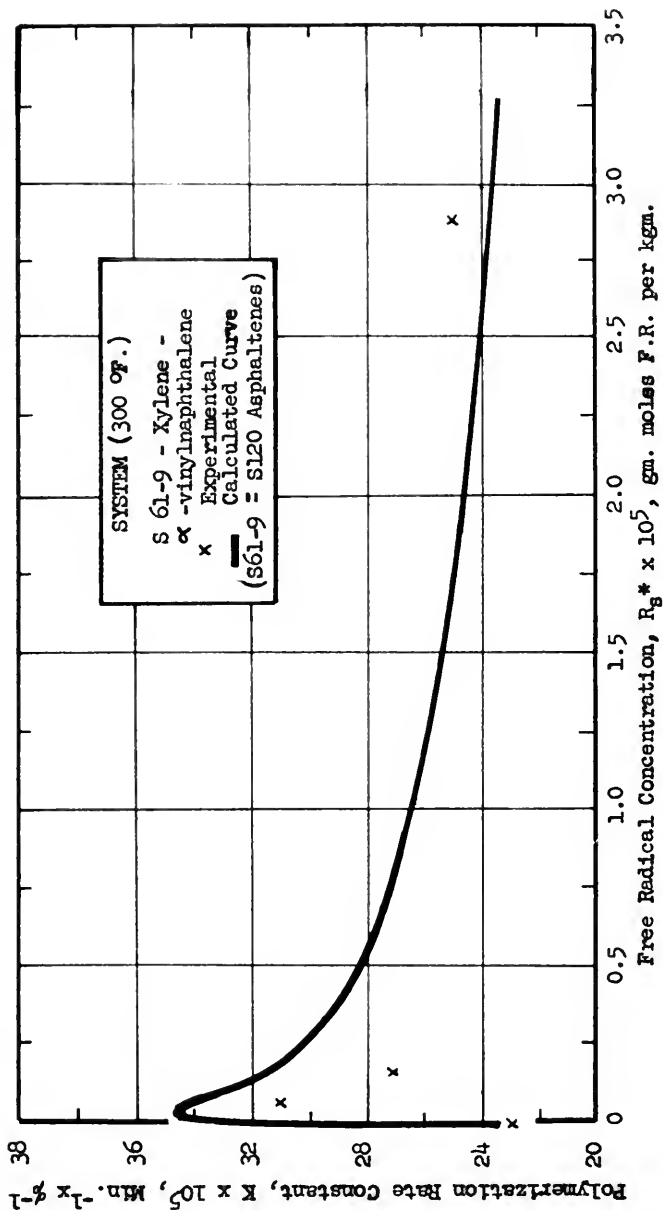


Figure 21, A comparison of theory with experiment.

varying the parameters systematically. The value of the parameters which are considered to yield the best fit to the experimental data are presented in Table 19.

TABLE 19, CONSTANTS DETERMINED FOR THE THEORETICAL
POLYMERIZATION RATE CONSTANT EQUATION

Note: The values for the constants cited are to be used when R_g^* has the units, Gm. moles free radicals per kgm. of system and when K has the units, $(\% \text{ Monomer})^{-1}(\text{Minutes})^{-1}$.

System	Constant A	Constant B	Constant C	Constant D
Styrene - Xylene - S119	290	9.5×10^{-9}	1.90×10^{-14}	0.7
Styrene - Xylene - S119 Asphaltenes	290	9.5×10^{-9}	1.90×10^{-14}	0.7
Styrene - Xylene - S120	547	8.1×10^{-9}	5.35×10^{-15}	0.7
Styrene - Xylene - S120 Asphaltenes	547	8.1×10^{-9}	5.35×10^{-15}	0.7
α -vinyl naphthalene - Xylene - S120 Asphaltenes	5470	3.2×10^{-8}	1.77×10^{-15}	0.9

The order of magnitude of the maximum acceleration of the polymerization rate for the α -vinyl naphthalene systems, was only about twice the expected experimental error. It is possible that better

agreement with the theory might have been obtained with more experimentation.

This agreement between the theoretically calculated values and experimental values allows the plausibility of the assumed mechanism of interaction of stabilized free radicals in polymer systems. The results actually can be applied with reasonable certainty to the systems studied but it should be possible to apply these ideas to similar phenomena that may occur in other systems. It was noted earlier that vinyl-2-ethylhexanoate had no observable polymerization rate of its own, or in the presence of asphaltenes from S 120. However, in the presence of benzoyl peroxide polymerization occurred easily. It is believed that this also lends strength to the manner in which it has been assumed that stabilized free radicals were capable of interacting in polymer systems. If the stabilized free radicals were capable of interacting in the manner of active free radicals, an effect similar to that observed for benzoyl peroxide with this monomer should have been observed for the asphaltene from S 120.

Mack has made the following claim in a U. S. Patent: when vinyl compounds are reacted in asphalt systems, catalyzed by a small amount of an organic peroxide, reaction with the asphaltene fraction occurs. This claim has been based on the observation that 20 - 30 percent of the asphaltenes which are normally insoluble in naphtha become soluble after reaction with the vinyl compounds.(60)

D. Aggregation and Solvation of the Asphaltenes

It has been tentatively suggested that the overall polymerization rate constant is affected by the concentration of free radicals. It can be seen from Figure 20, page 102, which presents a curve calculated from the theoretical equation correlating this polymerization rate constant, K , with free radical concentration, that K approaches a constant value in an asymptotic manner as the free radical concentration is increased. In Figure 15, page 79, however, it may be seen that there is an upward trend for K as the asphalt concentration approaches 90 percent. This is, of course, not in accordance with an interpretation that the free radical concentration is a linear function of the asphalt concentration. Earlier, in the discussion of theory, evidence was cited which indicated that the total concentration of free radicals in asphalt solutions was nearly proportional to the asphalt concentration. Evidence was also cited to show that dissociation of unstable molecules to form free radicals as the asphalt solutions become more dilute probably does not occur. Thus far, the results appear to be contradictory.

It is believed that this apparently anomalous behavior can be explained on the basis of two related phenomena whose consequences are observable in asphalt systems, namely, that of solvation of the asphaltenes preferentially by the highest molecular weight molecules of the resins and association of the asphaltenes themselves. The majority of the stabilized free radicals are concentrated in the asphaltene fraction. This has been shown by

polymerization experiments since the maximum acceleration occurred at concentrations of asphaltenes which were lower than those of the source asphalts. If it is assumed that association and solvation of the free radical containing (asphaltene) portion of the asphalt does occur, it can be understood that the quantity of free radicals available for reaction with the monomeric portion of the reaction system (when monomers have been added) will not necessarily equal the total quantity of free radicals intrinsically present in the asphalt. In other words, a portion of the free radicals will be restricted from entering into chemical reaction with the polymerizing system by an essentially mechanical barrier. This implies that it is entirely feasible that the concentration of stabilized free radicals available for reaction may, in fact, decrease even though the total concentration of stabilized free radicals in the whole of the asphalt system may increase as the asphalt concentration is increased. Consequently, if the available stabilized free radical concentration, named R_g^* in previous discussions, is reduced sufficiently, the rate constant, K , should be expected to rise as did occur for polymerization in the asphalts, S 119 and S 120 (Figure 15).

Neppe has reviewed the chemistry and rheology of asphaltic bitumen in a recent publication.(69) Here evidence based on measurements of complex flow behavior, electron microscopic examination, oxidation of the asphaltenes, and correlation of physical properties allows the statement to be made that:

"There is general agreement that these materials [asphalts] are colloidal systems consisting of micelles dispersed in an oily medium."

He indicates also that there is general acceptance that these micelles, which largely constitute the asphaltene fraction, are lyophobic nuclei surrounded by shells or successive layers of material of gradually decreasing molecular weight and carbon content or aromaticity. In dilute solution it is believed that these adsorbed layers are dissolved away, allowing precipitation to occur in petroleum ether (n-pentane for example) and flocculation to occur in solution with good solvents such as carbon tetrachloride. Figure 22 is a model representing the manner in which solvation of the asphaltene micelle occurs, as conceived by Pfeiffer.(74) The process of air blowing presumably gradually reduces the quantity of material in the continuous phase causing a gradual increase in the aggregation of micelles.

It seems reasonable to expect that such phenomena as just described be a gradual function of the amount of solvent present. Indeed, this is true at least for the phenomenon of asphaltene aggregation. Winniford states that:

"Aggregation of asphaltenes in concentrated systems is a well-known phenomenon. The precipitation of asphaltenes by poor solvents such as pentane obviously involves aggregation of an extreme type. . . . In concentrated solutions the concept of aggregation of asphaltenes is, therefore, broadly accepted; but it is more difficult to accept the postulate that asphaltenes exist as aggregates, even in dilute solutions in supposedly good solvents."

Further conclusions by Winniford were that aggregation in dilute solution with good solvents does occur and that this aggregation may

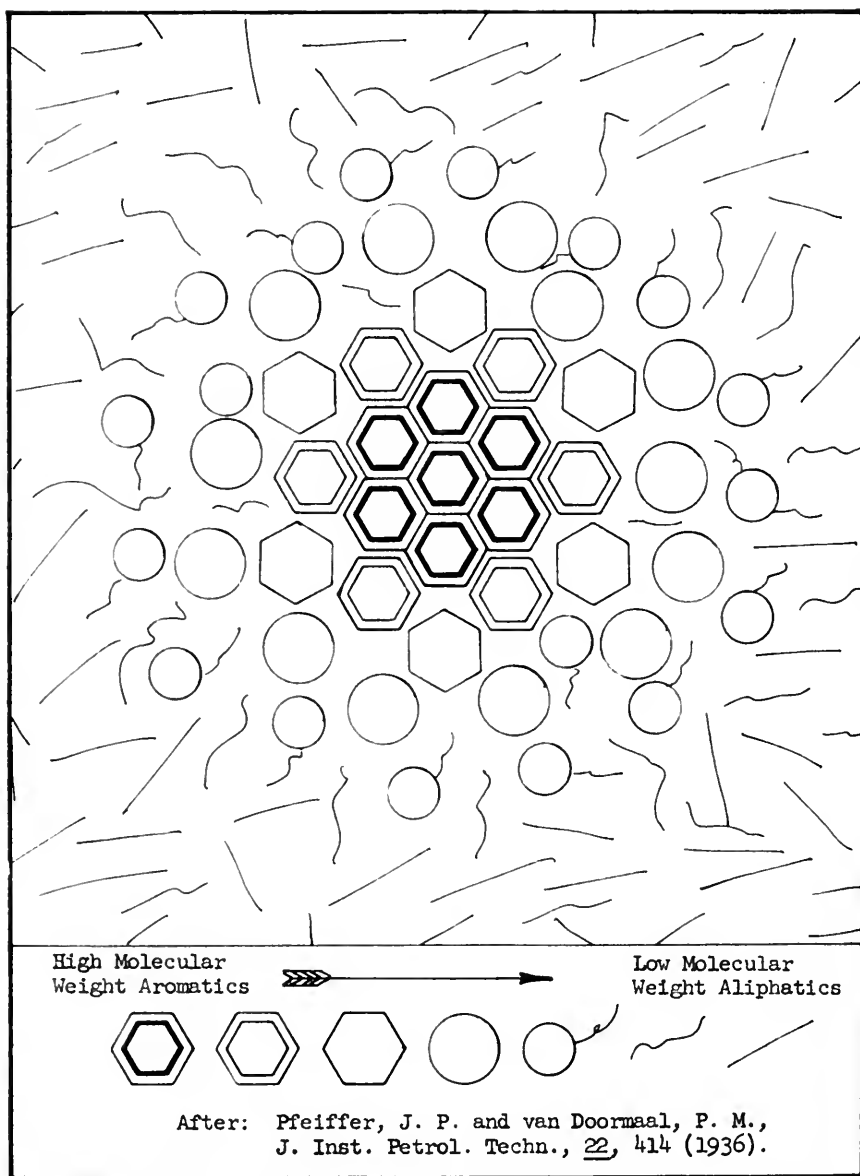


Figure 22, An asphaltene model showing the solvation effect occurring in relatively concentrated asphalt systems.

be expected to increase as the quantity of solvent is reduced.

(103) Heithaus has made a study of the significance of asphaltene peptization. It was suggested that aggregation of the asphaltenes in concentrated systems is at least as important to the properties of the system as the changes in molecular configuration resulting from differences in the solvating power of the continuous phase.

(46)

With the phenomena of asphaltene aggregation and solvation in concentrated systems fairly well established, further examination of the experimental data at high asphalt concentration will continue. In Figure 16, page 81, data is presented showing the effect that air blowing the residuum S 119 had on the rate constant, K. It can be seen that K determined in polymerization runs on the air-blown asphalt, R60-11, never attains as low a value as in those for the asphalt S 119. This asphalt contains 39.4 percent asphaltenes, whereas S 119 contains only 2.6 percent. Schweyer and Bransford have reported that an air-blown asphalt prepared from S 119, the Gulf Coast naphthenic residuum, has a much greater degree of complex flow than S 119 had originally before air-blowing.(85) These facts are in accord with the ideas just discussed. Although it can not be definitely shown by these data, they may indicate that the asphalt R60-11 has had some reduction in the overall concentration of stabilized free radicals as a result of saturation of some of the radicals during the polymerization caused by the air-blowing operation. There has not been adequate study of this point to justify further comment.

VII. CONCLUSIONS

1) The vinyl compounds studied have polymerization rates in asphaltic media that may be correlated by means of a rate equation that is second order in monomer concentration.

2) The effect of temperature on the polymerization rate of a styrene asphalt system can be correlated by means of the Arrhenius equation. The system S 119 - styrene has an overall energy of activation that is 20,700 cal. per gm. mole. This is approximately the same as reported for other styrene solvent systems. The asphalts studied do not appear to greatly affect the overall energy of activation. (The activation energy of the individual reaction steps has not been determined.)

3) There are constituents concentrated in the asphaltene fraction of asphalts that are largely responsible for the interaction observed. It has been shown in a substantial manner that these components may be stable free radicals. The possibility that free radicals are concentrated and do exist in this fraction of the asphalts studied is confirmed.

4) A mechanism has been presented and an equation derived that correlates the effect of the variable stabilized free radical concentration. The essential feature of this mechanism is that these free radicals initiate polymerization via a ter-molecular reaction involving the stable free radical and two monomer molecules

and that they terminate chains via a ter-molecular reaction involving a stable free radical, active free radical and monomer molecule.

5) Stabilized free radicals from the asphalts studied have inhibiting and catalytic properties for the monomers, styrene and α -vinyl-naphthalene. At 300 °F. competition between these two effects results in a maximum acceleration of the polymerization rate at low concentration of the asphalts containing stable free radicals.

6) Because of asphaltene aggregation and solvation in concentrated asphalt systems, the effective free radical concentration available for interaction with polymerizing monomers appears to be limited.

7) A novel method of olefin analysis has been developed that can be used to obtain the quantity of vinyl-type monomers in complex asphaltic systems. By hydrogenation of the monomer selectively, this result can be achieved.

8) Free radical content of the asphaltic materials studied has been determined by electron spin evaluation. It appears to be of the order of 10^{16} to 10^{17} free radicals per gram.

VIII. SUMMARY

This research has been undertaken to establish a better understanding of the fundamental aspects of the manner in which asphalt affects vinyl monomer solvent systems. Through a study of the polymerization process of vinyl monomers and a kinetic analysis of the rate of polymerization observed for the various systems studied, it has been concluded that stabilized free radicals, which are present in asphalt residua, influence the course of the reaction.

Several typical petroleum residua, representing a wide range of types normally encountered, were the asphalt material used in this study. A Gulf Coast naphthenic residuum and an East Central Texas residuum, which represent residua of low and high asphaltene content, respectively, have been studied extensively. The monomer used principally has been vinyl benzene. These studies have also included vinyl-2-ethylhexanoate and α -vinyl naphthalene.

Polymerizations were conducted in an Aminco rocking autoclave equipped with automatic temperature control. Analysis of the monomer at any given time during a polymerization run is achieved by a selective micro-hydrogenation. In this investigation, the parameters monomer concentration, asphalt concentration, asphaltene concentration and reaction temperature have been varied over the ranges as follows: monomer concentration: 2 - 15 percent; asphalt concentration: 0 - 90 percent; asphaltene concentration: 0 - 18 percent; and temperature: 200 - 450 °F.

It has been shown that the temperature effect on the polymerization rate of the Gulf Coast naphthenic residuum, vinylbenzene system may be correlated by means of Arrhenius' equation, using an overall energy of activation of about 20,700 cal. per gm. mole. This compared closely with the energy of activation cited in the literature for this monomer in other solvents.

An equation has been developed from a hypothesis describing the polymerization process, which can be used to calculate the reaction rate as a function of monomer concentration and stabilized free radical concentration. By assuming a linear relation of free radical content of asphalt or asphaltene, the effect of these variables may be interpreted. This equation is as follows:

$$\begin{aligned} -d(M)/dT &= A \left((R^2 + BR^D + C)^{\frac{1}{2}} - R \right) M^2 \\ &= K (M)^2 \end{aligned}$$

Where: K has been set equal to the term in front of M^2 .

M is the monomer concentration.

A, B, C, D are empirical constants resulting from grouping the constants of the individual reaction rate steps of the assumed mechanism.

The essential feature of this proposed mechanism is that free radicals present in asphalts initiate polymerization via a ter-molecular reaction involving the stable free radical and two monomer molecules and that they terminate chains via a ter-molecular reaction involving a stable free radical, active free radical and monomer molecule.

The I. B. M. 650 digital computer has been used to estimate proper values of the constants A, B, C and D by systematically varying these constants and comparing the calculated curves with the experiment curves. Agreement for the curves has been sufficient to indicate the probable correctness of the hypothesis presented.

An interpretation developed from these results is that the stabilized free radicals from the asphalts studied have inhibiting and catalytic properties. At 300 °F. competition between these two effects results in a maximum acceleration of the polymerization rate at low concentration of the asphalts containing the free radicals.

Because of asphaltene aggregation and solvation in concentrated asphalt systems, the effective free radical concentration available for interaction with polymerizing monomer appears to be limited.

Free radical content of the asphaltic materials has been reported from outside determinations by electron spin evaluation. It appears to be of the order of 10^{16} to 10^{17} free radicals per gram.

IX. SUGGESTED FUTURE WORK

In the discussion of results, it was suggested that the asphalt R60-11 which had been air-blown at 500 °F., may have a concentration of free radicals less than the original asphalt. This might be explained by assuming that the broken edge bonds (stabilized free radicals) are saturated as a result of the polymerization of ring clusters during the air-blowing process at this temperature. Holmgren has shown that the hardening during the air-blowing process occurs via a mechanism involving polymerization, dehydrogenation and decarbonization.(48) It may be possible that asphalts air-blown at considerably higher temperatures, say 750 °F. and up, have poor service performance in comparison with asphalts prepared at the lower temperatures because of a cracking phenomenon which produces stabilized free radicals. Previous discussions have demonstrated that the formation of stabilized free radicals in pyrolytic carbons is favored as the temperature is increased to 550 °C. It is believed that a study of stabilized free radicals in connection with this process may possibly yield ultimately a better understanding of the variables responsible for the service behavior of air-blown asphalts, since the stabilized free radicals may take an active part in the reactions causing degradation under service conditions.

X. NOMENCLATURE

<u>Symbol</u>	<u>Definition</u>
1,2,3,...,n,n-1	Subscript denoting the number of monomer units affixed to a growing polymer radical, with n the last monomer unit to be affixed.
'	Denotes corrected values of K and N.
a	Subscript denoting all active free radicals.
A	Arrhenius frequency or proportionality factor.
A, B, C, D	Empirical constants in the kinetic equation for the overall polymerization rate constant. (see page 65)
b	Subscript denoting hydrogenation unit burette.
c	Subscript denoting a radical formed in the initiation phase.
c _f	A conversion factor defined by equation 29.
d _γ	Chain distance shown on the asphaltene model, Å.
d _M	Interlayer distance shown on the asphaltene model, Å.
f	Subscript denoting final conditions.
g	Spectroscopic splitting factor.
h	Subscript denoting hydrogenation system.
H	Arrhenius activation energy.
i	Subscript denoting <u>i</u> th. item or initial conditions.
j	Subscript denoting hydrogenation unit water jacket.

<u>Symbol</u>	<u>Definition</u>
k	Reaction mechanism rate constant identified by proper subscript.
K	Overall polymerization rate constant, empirical or theoretical.
L_a	Diameter of the aromatic sheets shown on the asphaltene model, Å.
L_c	Diameter of the aromatic clusters perpendicular to the plane of the sheets, Å.
m	Monomer molecular weight.
M	Monomer molecules or monomer concentration.
n	Gram moles of gas or a subscript denoting the number of monomer units attached to a polymer.
N	Slope of Arrhenius plot.
o	Subscript denoting change from initial to final conditions.
p	Partial pressure or subscript identifying a propagation rate constant.
P	Pressure.
q_A	The specie quotient of a system containing species A, defined by equation 41.
r	Subscript denoting hydrogenation reaction flask volume.
R	Ideal gas law constant.
R^*	A free radical or free radical concentration.
s	Subscript denoting stabilized free radicals.
S	Subscript denoting solvent vapor.
t	Subscript identifying termination rate constant.
T	Time or absolute temperature.
V	Volume.
W	Sample weight hydrogenated.

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XII. APPENDICES

APPENDIX A

POLYMERIZATION RUN RAW DATA

TABLE 20. POLYMERIZATION RUN DATA FOR RUNS WITH THE GULF CCAST NAPHTHENIC RESIDUUM (SL19), STYRENE AND XYLENE

Run Number	% S119	Charge Conditions % Styrene % Xylene	Temperature, °F.
R61-48	2.91	10.0	87.1 300
	Elapsed time, min.		90
	Wt. % styrene remaining		8.91
R61-3	4.97	9.94	85.1 300
	Elapsed time, min.		21
	Wt. % Styrene remaining		9.78
R61-6	4.99	10.1	84.9 300
	Elapsed time, min.		45
	Wt. % Styrene remaining		10.01
R61-7	14.9	10.0	75.1 300
	Elapsed time, min.		30
	Wt. % Styrene remaining		9.85
R61-2	29.8	10.1	60.1 300
	Elapsed time, min.		25
	Wt. % Styrene remaining		10.08

TABLE 20, CONTINUED

Run Number	Charge Conditions		Temperature, °F.
	% S119	% Styrene % Xylene	
R61-8	36.9	10.1 53.0	300
	Elapsed time, min.		29
	Wt. % Styrene remaining		8.68
R61-1	60.6	8.98 30.4	300
	Elapsed time, min.		20
	Wt. % Styrene remaining		8.49
	Elapsed time, min.		2510
	Wt. % Styrene remaining		4.28
R60-10	89.2	10.8	200
	Elapsed time, min.		99
	Wt. % Styrene remaining		10.20
	Elapsed time, min.		6810
	Wt. % Styrene remaining		9.49
R60-9	89.8	10.2	250
	Elapsed time, min.		11
	Wt. % Styrene remaining		9.32
	Elapsed time, min.		2623
	Wt. % Styrene remaining		8.15

TABLE 20, CONTINUED

Run Number	Charge Conditions		Temperature	
	% S119	% Styrene % Xylene	°F.	
R60-5	90.0	9.96	300	
	Elapsed time, min.			
	Wt. % Styrene remaining		6	25
			9.20	9.07
R60-4	Elapsed time, min.			
	Wt. % Styrene remaining		540	664
			7.13	6.78
	90.0	10.0	400	
R60-3	Elapsed time, min.			
	Wt. % Styrene remaining		8	22
			9.36	7.01
	90.0	9.96	400	
R60-5	Elapsed time, min.			
	Wt. % Styrene remaining		330	531
			1.88	1.45
	90.0	9.96	400	
R60-3	Elapsed time, min.			
	Wt. % Styrene remaining		3	18
			7.93	7.01
	90.0	9.96	400	
R60-5	Elapsed time, min.			
	Wt. % Styrene remaining		300	25
			7.83	7.07
	90.0	9.96	400	
R60-4	Elapsed time, min.			
	Wt. % Styrene remaining		300	25
			7.83	7.07
	90.0	9.96	400	
R60-3	Elapsed time, min.			
	Wt. % Styrene remaining		300	25
			7.83	7.07
	90.0	9.96	400	

TABLE 21. POLYMERIZATION RUN DATA FOR RUNS WITH THE EAST CENTRAL TEXAS RESIDUUM (SL20), STYRENE AND XYLENE

Run Number	Charge Conditions % S120 % Styrene % Xylene	Temperature °F.
R61-24	0.266 10.0 89.7	300
	Elapsed time, min. Wt. % Styrene remaining	
R61-23	0.839 10.1 89.1	300
	Elapsed time, min. Wt. % Styrene remaining	
R61-22	1.63 9.93 88.5	300
	Elapsed time, min. Wt. % Styrene remaining	
R61-18	3.21 9.92 86.9	300
	Elapsed time, min. Wt. % Styrene remaining	
R61-17	6.39 10.1 83.5	300
	Elapsed time, min. Wt. % Styrene remaining	

TABLE 21, CONTINUED

Run Number	Charge Conditions		Temperature °F.									
	% StI20 % Styrene	% Xylene										
R61-31	29.9	10.1	60.0	300								
	Elapsed time, min.											
	Wt. % Styrene remaining				110	543	922	1374	1752	2298	2298	4.41
					9.00	7.97	5.96	5.73	5.08			
R61-32	60.0	10.0	30.0	300								
	Elapsed time, min.											
	Wt. % Styrene remaining				48	490	887	1306	1748	2122	2122	4.62
					9.05	7.81	6.47	5.73	4.77			
R61-33	75.3	9.47	15.2	300								
	Elapsed time, min.											
	Wt. % Styrene remaining				93	370	942	1509	1787	2381	2381	3.98
					8.37	7.50	6.22	4.93	4.54			
R61-35	84.2	10.0	5.8	300								
	Elapsed time, min.											
	Wt. % Styrene remaining				59	467	1014	1490	1928	2402	2402	3.36
					9.26	7.14	5.52	4.46	3.92			
R60-19	89.0	9.95		300								
	Elapsed time, min.											
	Wt. % Styrene remaining				96	500	1039	1426	2011	2500	2500	2.57
						6.43	4.63	3.99	3.53			

TABLE 21, CONTINUED

Run Number	Charge Conditions		Temperature					
	% SI20	% Styrene	% Xylene	°F.				
R60-22	89.8	10.2		300				
	Elapsed time, min.							
	Wt. % styrene remaining				98	471	772	1269
					8.41	6.98	5.52	4.68
								1725
								3.82
								2185
								3.41
								2750
								2.66
R60-21	90.0	10.0		400				
	Elapsed time, min.							
	Wt. % Styrene remaining				36	93	157	228
					6.36	3.90	3.12	2.34
								296
								2.00
								363
								1.43
								420
								1.04

TABLE 22, POLYMERIZATION RUN DATA FOR RUNS WITH 500°F.
AIR BLOWN SIL9 (R60-11), STYRENE AND XYLENE

Run Number	Charge Conditions		Temperature,					
	% R60-11	% Styrene	% Xylene	°F.				
R61-45	0.573	9.87	89.5	300				
	Elapsed time, min.			147	639	1207	1674	2238
	Wt. % Styrene remaining			8.99	6.86	5.28	4.52	3.89
R61-46	1.57	9.93	88.5	300				
	Elapsed time, min.			141	693	1279	1679	1724
	Wt. % Styrene remaining			9.32	6.48	4.80	4.11	4.22
R61-47	5.02	10.1	84.9	300				
	Elapsed time, min.			90	511	949	1424	1897
	Wt. % Styrene remaining			9.69	7.04	5.43	4.34	3.51
R61-49	17.0	9.90	73.1	300				
	Elapsed time, min.			89	525	878	1429	1841
	Wt. % Styrene remaining			9.42	7.37	6.03	4.69	3.99
R61-54	54.8	10.1	35.1	300				
	Elapsed time, min.			205	740	1285	1667	2200
	Wt. % Styrene remaining			9.99	7.07	5.40	4.67	3.73

TABLE 22, CONTINUED

Run Number	Charge Conditions		Temperature, °F.					
	% R60-11	% Styrene	% Xylene					
R60-13	89.9	10.1						
R60-12	89.9	10.1						
R60-14	90.1	9.90						

R60-13	Elapsed time, min.	122	264	444	902	1188	1528	2093
	Wt. % Styrene remaining	7.66	7.84	7.35	5.57	4.94	4.17	3.57
R60-12	Elapsed time, min.	81	208	262	392	502	582	657
	Wt. % Styrene remaining	4.12	2.09	1.47	1.14	0.830	0.802	0.637
R60-14	Elapsed time, min.	36	66	147	225	314		
	Wt. % Styrene remaining	2.78	1.56	0.977	0.570	0.580		

TABLE 23, POLYMERIZATION RUN DATA FOR RUNS WITH VARIOUS
PETROLEUM COMPONENTS AND STYRENE

Run Number	Charge Conditions			Temperature,		
	Material Used	% Material Used	% Styrene	of.		
R60-15(a)	S60-1	90	10	200		
	(S60-1 is petrolatum)					
	Elapsed time, min.					
	Wt. % Styrene remaining					
			96	1121	2744	4234
			9.77	8.76	7.47	6.27
						5.63
						6881
						4.88
R60-20	S117	90	10	300		
	(S117 is the East Texas Asphalt Base Residuum)					
	Elapsed time, min.					
	Wt. % Styrene remaining					
			58	457	852	1403
			8.51	7.58	5.77	4.67
						4.06
						2430
						3.04
R60-18	S118	90	10	300		
	(S118 is the South Texas Heavy Asphalt Base Residuum)					
	Elapsed time, min.					
	Wt. % Styrene remaining					
			70	451	681	1108
			8.87	7.18	7.27	5.97
						5.32
						1785
						4.64
						2087
						4.33

(a) A definite precipitation of polymer occurred on the interior of the autoclave during this run.

TABLE 24, CONTINUED

Run Number	Charge Conditions		Temperature							
	% S61-6	% Styrene	% Xylene	°F.						
R61-10	4.97	10.2	84.8	300						
	Elapsed time, min.			80	428	758	1205	1599	2061	2485
	Wt. % Styrene remaining			10.02	9.85	8.87	7.76	6.99	6.13	5.77
R61-36	12.87	9.89	77.2	300						
	Elapsed time, min.			64	548	1088	1533	2025	2410	
	Wt. % Styrene remaining			9.75	9.40	8.46	7.67	6.67	6.18	

TABLE 25, POLYMERIZATION RUN DATA FOR RUNS WITH ASPHALTENES DERIVED FROM
S120 THE EAST CENTRAL TEXAS RESIDUUM (S61-9), STYRENE AND XYLENE

Run Number	Charge Conditions		Temperature					
	% S61-9	% Styrene % Xylene	of.					
R61-38	0.268	9.96	89.8	300				
	Elapsed time, min.		128	561	1012	1423	1822	2465
	Wt. % Styrene remaining		9.50	6.43	4.25	3.33	2.75	2.12
R61-37	0.653	10.1	89.2	300				
	Elapsed time, min.		161	659	1117	1569	1845	2385
	Wt. % Styrene remaining		9.56	5.58	3.65	2.92	2.64	2.19
R61-34	4.02	9.89	86.1	300				
	Elapsed time, min.		14	555	1042	1503	1974	2331
	Wt. % Styrene remaining		9.44	7.05	5.30	5.08	4.53	4.07
R61-55	4.01	9.91	86.1	300				
	Elapsed time, min.		100	484	911	1300	1770	2390
	Wt. % Styrene remaining		9.85	7.02	6.25	4.97	4.61	3.45
R61-39	18.1	9.83	72.1	300				
	Elapsed time, min.		68	517	1025	1439	1984	2467
	Wt. % Styrene remaining		9.92	8.43	6.64	5.81	4.92	4.42

TABLE 26. POLYMERIZATION RUN DATA FOR RUNS WITH ASPHA'TENES DERIVED FROM SL20 THE EAST CENTRAL TEXAS RESIDUUM (S61-9), α -VINYLNAPHTHALENE AND XYLENE

Run Number	Charge Conditions		Temperature °F.
	% S61-9 Naphthalene	% α -Vinyl Xylene	
R61-50	0.0	13.5	300
	Elapsed time, min.		
	Wt. % α -Vinyl naphthalene remaining	58	1174
		11.36	2.88
		417	782
		5.59	3.81
			1462
			2.36
R61-51	0.299	13.4	300
	Elapsed time, min.		
	Wt. % α -Vinyl naphthalene remaining	17	868
		11.72	3.04
		238	564
		8.28	4.16
			1159
			2.39
			1480
			1.87
R61-52	0.745	13.4	300
	Elapsed time, min.		
	Wt. % α -Vinyl naphthalene remaining	21	792
		12.26	3.43
		267	521
		6.74	4.55
			1047
			2.83
			1387
			2.25
R61-53	15.7	13.5	300
	Elapsed time, min.		
	Wt. % α -Vinyl naphthalene remaining	31	1030
		11.37	3.04
		270	617
		6.34	4.32
			1385
			2.35

TABLE 27, POLYMERIZATION RUN DATA FOR RUNS WITH 1,1-DIPHENYL-2-PICRYLHYDRAZYL, STYRENE AND XYLENE

Run Number	Charge Conditions			Temperature °F.				
	%S61-11	% Styrene	% Xylene					
R61-19	0.0018	10.0	90.0	300				
	Elapsed time, min.				39	254	642	1057
	Wt. % Styrene remaining				9.28	8.60	7.33	6.53
							1449	1930
							5.62	5.03
								2476
								4.47
R61-29	0.0026	10.0	90.0	300				
	Elapsed time, min.				111	565	999	1398
	Wt. % Styrene remaining				9.27	7.68	6.24	5.49
							1842	2302
							4.97	4.31
R61-25	0.0028	10.1	89.9	300				
	Elapsed time, min.				35	463	958	1437
	Wt. % Styrene remaining				9.90	7.66	5.97	5.12
							1896	2424
							4.32	3.73
R61-26	0.0029	10.0	90.0	300				
	Elapsed time, min.				39	404	942	1414
	Wt. % Styrene remaining				9.23	7.72	5.83	4.82
							1740	2363
							4.44	3.69
R61-27	0.0030	10.0	90.0	300				
	Elapsed time, min.				112	182	533	974
	Wt. % Styrene remaining				8.92	8.58	7.57	6.43
							1152	1658
							6.23	5.13
								2153
								4.71

TABLE 27, CONTINUED

Run Number	Charge Conditions		Temperature						
	% S61-11	% Styrene	% Xylene	°F.					
R61-30	0.0033	10.1	89.9	300					
	Elapsed time, min.								
	Wt. % Styrene remaining				95	515	963	1420	1803
					9.02	7.48	6.08	5.68	4.67
R61-21	0.0038	9.66	90.3	300					
	Elapsed time, min.				83	524	1033	1392	1899
	Wt. % Styrene remaining				9.71	8.33	6.78	5.73	4.98
R61-28	0.0074	10.1	89.9	300					
	Elapsed time, min.				11	577	1030	1534	2060
	Wt. % Styrene remaining				9.60	8.31	7.02	5.70	5.14
R61-20	0.018	9.88	90.1	300					
	Elapsed time, min.				37	514	926	1396	2076
	Wt. % Styrene remaining				9.92	8.73	7.54	6.63	5.62
									2758
									4.51

APPENDIX B

CALCULATED VALUES DETERMINED FOR THE
OVERALL POLYMERIZATION RATE CONSTANT

APPENDIX B

CALCULATED VALUES DETERMINED FOR THE OVERALL POLYMERIZATION RATE CONSTANT

System: Styrene - Xylene - S 119 or S 61-6 (300 °F.)

Empirically Determined Constants Used: $A = 290$, $B = 9.5 \times 10^{-9}$, $C = 1.90 \times 10^{-14}$, $D = 0.70$

$R_p \times 10^5$, $\frac{\text{gm. moles F.R.}}{\text{kgm. system}}$ 0.0 0.01 0.03 0.07 0.10 0.50 0.70 1.0 3.0

$K \times 10^5$, $\text{min.}^{-1} \times \% \text{ monomer}^{-1}$ 4.0 8.3 8.9 8.3 7.9 5.3 4.8 4.3 3.1

System: Styrene - Xylene - S 120 or S 61-9 (300 °F.)

Empirically Determined Constants Used: $A = 547$, $B = 8.1 \times 10^{-9}$, $C = 5.35 \times 10^{-15}$, $D = 0.70$

$R_p \times 10^5$, $\frac{\text{gm. moles F.R.}}{\text{kgm. system}}$ 0.0 0.01 0.03 0.07 0.10 0.50 0.70 1.0 3.0

$K \times 10^5$, $\text{min.}^{-1} \times \% \text{ monomer}^{-1}$ 4.0 13.3 14.4 14.5 12.7 8.6 7.8 7.0 5.1

System: α -vinyl naphthalene - Xylene - S 120 (300 °F.)

Empirically Determined Constants Used: $A = 5470$, $B = 3.2 \times 10^{-8}$, $C = 1.77 \times 10^{-15}$, $D = 0.90$

$R_p \times 10^5$, $\frac{\text{gm. moles F.R.}}{\text{kgm. system}}$ 0.0 0.01 0.03 0.07 0.10 0.50 0.70 1.0 3.0

$K \times 10^5$, $\text{min.}^{-1} \times \% \text{ monomer}^{-1}$ 23.0 36.1 36.3 34.7 33.8 29.2 28.2 27.2 24.4

APPENDIX C

FLATLAN OBJECT PROGRAM FOR THE I. B. M. 650 COMPUTER

FLATRAM OBJECT FOR THE I. B. M. 650 COMPUTER

		REG	C0001	C051				
1	C0051	NOP	C0001	C0001				
2	C0001	RAL		READ				
3		-RAL	A					
4		-RAL	B					
5		-RAL	C					
6		-RAL	D	C0012				
7	C0012	RAL		C062				
8		NOP	R					
9	C062	LDD		IMPY				
10		STL	C010					
11		RAL	C060					
12		NOP	R	D				
13	C030	LDD		SEXF				
14		STL	C019					
15		RAL	C059					
16		NOP	B	C019				
17	C069	LDD		IMPY				
18		STL	C030					
19		RAL	C070					
20		NOP	C010	C027				
21	C070	LDD		9ADD				
22		STL	C021					
23		RAL	C077					
24		NOP	C021	C				
25	C077	LDD		9ADD				
26		STL	C022					
27		RAL		SQRT				
28		-RAL	C022					
29		STL	C023					
30		RAL	C000					
31		NOP	C023					
32	C004	LDD		9ADD				
33		STL	C024					
34		RAL	C000					
35		NOP	A	C024				
36	C000	LDD		9IFY				
37		STL	C025					
38		LDD	C030					
39		STD	K					
40		LDD	C					
41		STD	X					
42		LDD	C039					
43		STD	R					

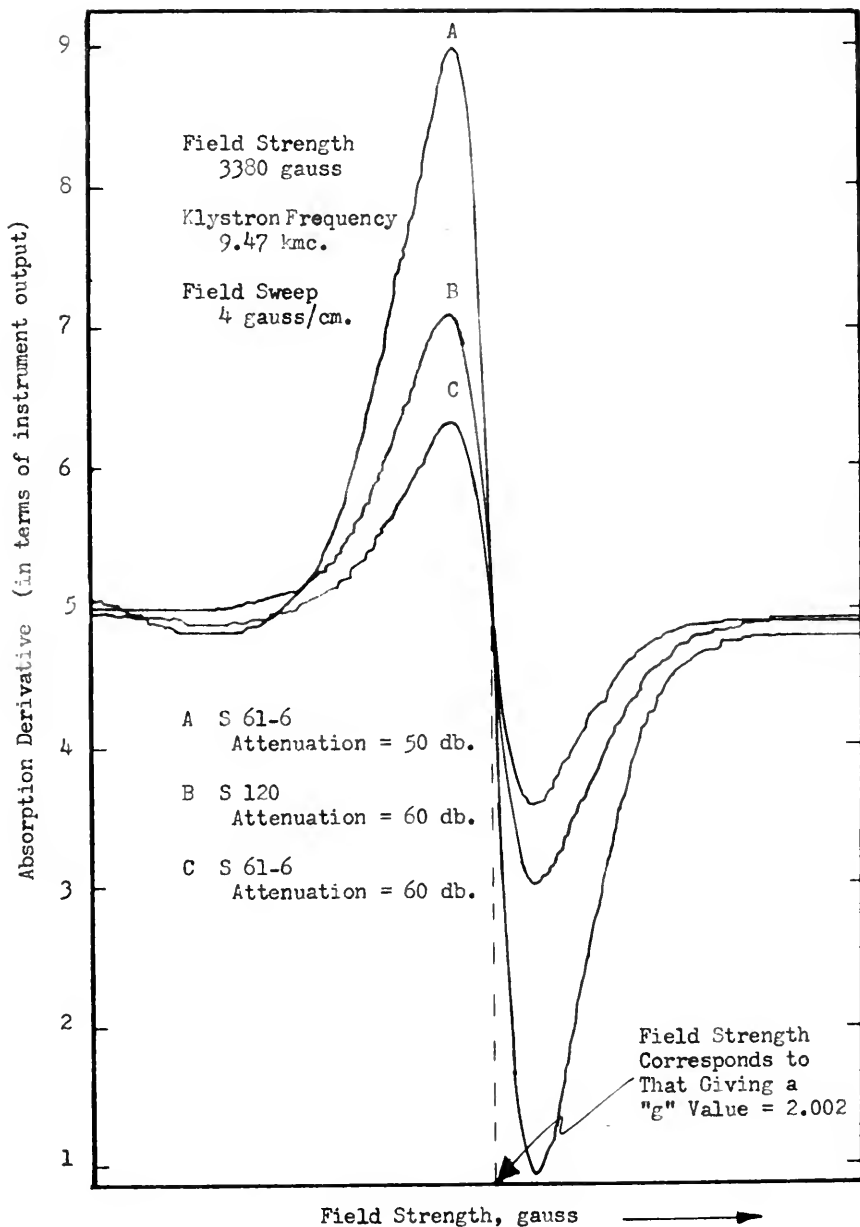
44		RAL							
45		-RAL							
46		-RAL							
47		-RAL	A						
48		-RAL	C						
49		-RAL	C						
50		-RAL	C						
51	1.11	RAL							
52		NOP	1010						
53	1.11	LDD							
54		STL	0818						
55		LDD	0818						
56		STD	0						
57		RAL							
58		NOP	1017						
59	1.18	LDD							
60		STL	0818						
61		LDD	0818						
62		STD							
63		RAL							
64		STL	A						
65	1.25	NOP	00117						
66	00017	RAL							
67		NOP	A						
68	1.27	LDD							
69		STL	0818						
70		RAL							
71		NOP	A						
72	1.31	LDD							
73		STL	0818						
74		RAL							
75		NOP	B						
76	1.34	LDD							
77		STL	0820						
78		RAL							
79		NOP	0818						
80	1.36	LDD							
81		STL	0821						
82		RAL							
83		NOP	0821						
84	1.42	LDD							
85		STL	0822						
86		RAL							
87		-RAL	0822						
88		STL	0823						
89		RAL							
90		NOP	0823						
91	1.49	LDD							
92		STL	0824						

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134		STL	1000	1000	1000
135	1000	STL	1000	1000	1000
136		STL	1000	1000	1000
137		STL	1000	1000	1000
138		STL	1000	1000	1000
139	0000	RAL	1000	1000	1000
140		RAL	1000	1000	1000
141		RAL	1000	1000	1000
142		RAL	1000	1000	1000
143		RAL	1000	1000	1000
144		RAL	1000	1000	1000
145		RAL	1000	1000	1000
146		RAL	1000	1000	1000
147		RAL	1000	1000	1000
148	1000	STL	1000	1000	1000
149		STL	1000	1000	1000
150		RAL	1000	1000	1000
151		RAL	1000	1000	1000
152	1000	STL	1000	1000	1000
153		STL	1000	1000	1000
154		STL	1000	1000	1000
155		STL	1000	1000	1000
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172		STL	1000	1000	1000
173		STL	1000	1000	1000
174		STL	1000	1000	1000
175		STL	1000	1000	1000
176		STL	1000	1000	1000
177		STL	1000	1000	1000
178		STL	1000	1000	1000
179		STL	1000	1000	1000
180		STL	1000	1000	1000
181		STL	1000	1000	1000
182		STL	1000	1000	1000
183		STL	1000	1000	1000
184		STL	1000	1000	1000

APPENDIX D

SAMPLE ELECTRON SPIN RESONANCE DERIVATIVE ABSORPTION CURVES
OF THE ASPHALT RESIDUA

SAMPLE ELECTRON SPIN RESONANCE DERIVATIVE ABSORPTION
CURVES OF THE ASPHALT RESIDUA

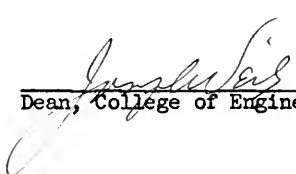


BIOGRAPHICAL SKETCH

Allen Edward Leybourne, III was born August 26, 1934, at Jacksonville, Florida. In this city he pursued his education, graduating from Andrew Jackson High School in June, 1952. In June, 1956, he received the degree of Bachelor of Science in Chemical Engineering from the University of Florida. After spending the summer as a chemist with Shell Chemical Company, Mr. Leybourne entered the Graduate School at Pennsylvania State University as a part-time student while being employed as a research assistant at the Petroleum Refining Laboratory. He completed his Master of Science degree in August, 1958, at this university and left to again pursue his education at the University of Florida. Since this time, except during the summer of 1960 when he worked for the Atlantic Refining Company in the Research and Development Department, Mr. Leybourne has continued his work toward the degree of Doctor of Philosophy. Mr. Leybourne is married to the former Margaret Cecile Fuller and is now the father of one son. He is a member of Phi Eta Sigma, Sigma Tau, and Alpha Chi Sigma fraternities.

This dissertation was prepared under the direction of the chairman of the candidate's supervisory committee and has been approved by all members of that committee. It was submitted to the Dean of the College of Engineering and to the Graduate Council, and was approved as partial fulfillment of the requirements for the degree of Doctor of Philosophy.

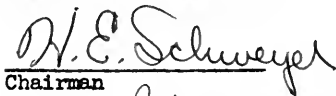
August 12, 1961.



Dean, College of Engineering

Dean, Graduate School

Supervisory Committee:



Chairman

